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MULTIFUNCTIONAL GEL-SILICA OPTICS

FINAL REPORT

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AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base, DC 20332

Grant No. AFOSR-91-0193

Period Covered

March 1, 1990 - December 31, 1993

Submitted by

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1/31/94	3. REPORT TYPE AND DATES COVERED Final 3/1/90 - 12/31/93	
4. TITLE AND SUBTITLE MULTIFUNCTIONAL GEL-SILICA OPTICS			5. FUNDING NUMBERS	
6. AUTHOR(S) L. L. Hench				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Florida 219 Grinter Hall Gainesville, FL 32611			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-94 0157	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC Building 410 Bolling AFB, DC 20332-6448			10. SPONSORING / MONITORING AGENCY REPORT NUMBER AFOSR-91-0193	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) High purity gel-silica matrices are produced using alkoxide sol-gel processing to form net-shape optical components with interconnected porosity. The porous optical matrices are impregnated with optically active polymers to produce multifunctional optical composites such as tunable dye lasers, scintillators, and photopolymerized 3-D gratings. Thus, the feasibility has been established for a new generation of multi-functional optical materials for sensors, detectors, waveguides, transpiration cooling, lasers, scintillators, multiplexers, etc.				
14. SUBJECT TERMS gel-silica, lasers, polymers, micro optics, diffractive optics, waveguides, porous matrices			15. NUMBER OF PAGES 70	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

REPORT QUANTITY AND DATES COVERED 3

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SECTION I

INTRODUCTION

a. MULTIFUNCTIONAL GEL-SILICA OPTICS OVERVIEW

RESEARCH TEAMS:

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University of Manchester, Physics Dept., Manchester, England
(Professor Terry King)

Loughborough University of Technology, Dept. of Physics, Loughborough, England
(Professor Nick Phillips)

Brunel, University of West London, Dept. of Chemistry, Uxbridge, England
(Dr. Carole (Perry) Harrison)

OBJECTIVE

To combine the functions of optically active organic molecules with the mechanical, thermal and radiation stability of porous gel-silica matrices thereby producing multifunctional optical composites with unique combinations of properties. The porous gel-silica matrices will provide the processability required for specific optical devices and the mechanical, thermal and radiation stability without requiring these features to be built into optically active organic structures. The porous matrices will also provide a controlled stereo-chemical environment for the organic molecules and the means for in-situ photopolymerization using laser illumination.

APPROACH

High purity gel-silica matrices are produced using alkoxide sol-gel silica processing to form net-shape optical components. The interconnected porosity is controlled to a very specific average size in the nanometer range by varying the sol-gel chemistry and aging of the gel network. The volume fraction of porosity is varied from 0.4 to 0.8 and the surface chemistry is controlled by altering the surface density of hydroxyl groups with various thermal processing schedules. Texture and surface chemistry of the matrices are characterized and monitored using a variety of analytical techniques including Raman and IR spectroscopy. Optically active organic molecules, such as laser dyes and photopolymers are impregnated into the optically transparent matrices using vacuum techniques resulting in a uniform distribution of the organics in an optically transparent and mechanically rigid component. No further thermal treatment is required so the structural stability of the organic molecules is not compromised. Because the matrices are optically transparent it is possible to expose photosensitive monomers within the matrices to laser light and photopolymerize them into 3-D patterns. Thus, complex optical structures and properties can be designed and achieved without masks or chemical processing.

Figures 1 and 2 summarize the inter-institutional, interdisciplinary approach taken in this program. Because of funding limitations several of the interactions initiated in the program were terminated along the way (Coles at University of Manchester and Midwinter and

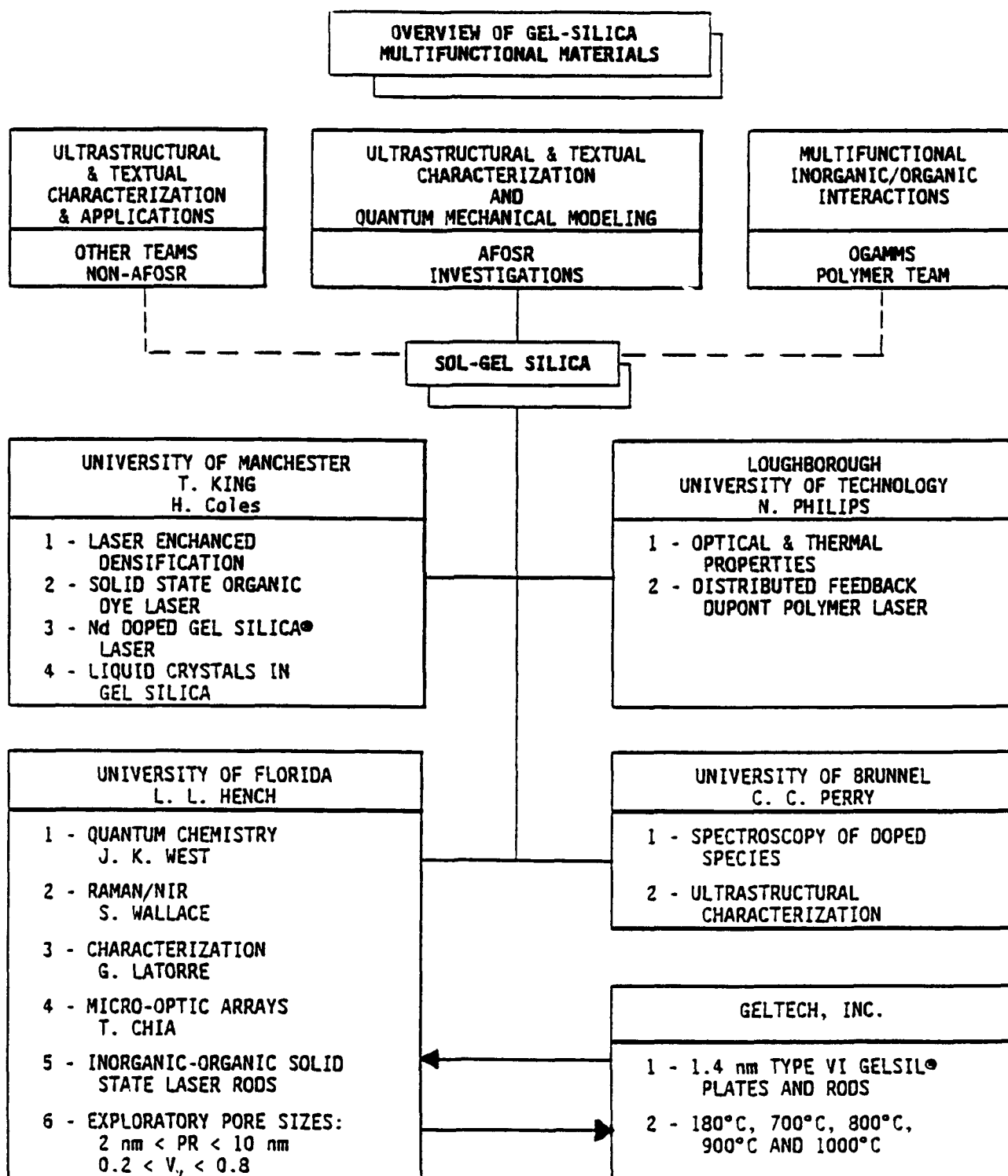


Figure 1

SYNERGISM OF US-UK COLLABORATIVE PROGRAM

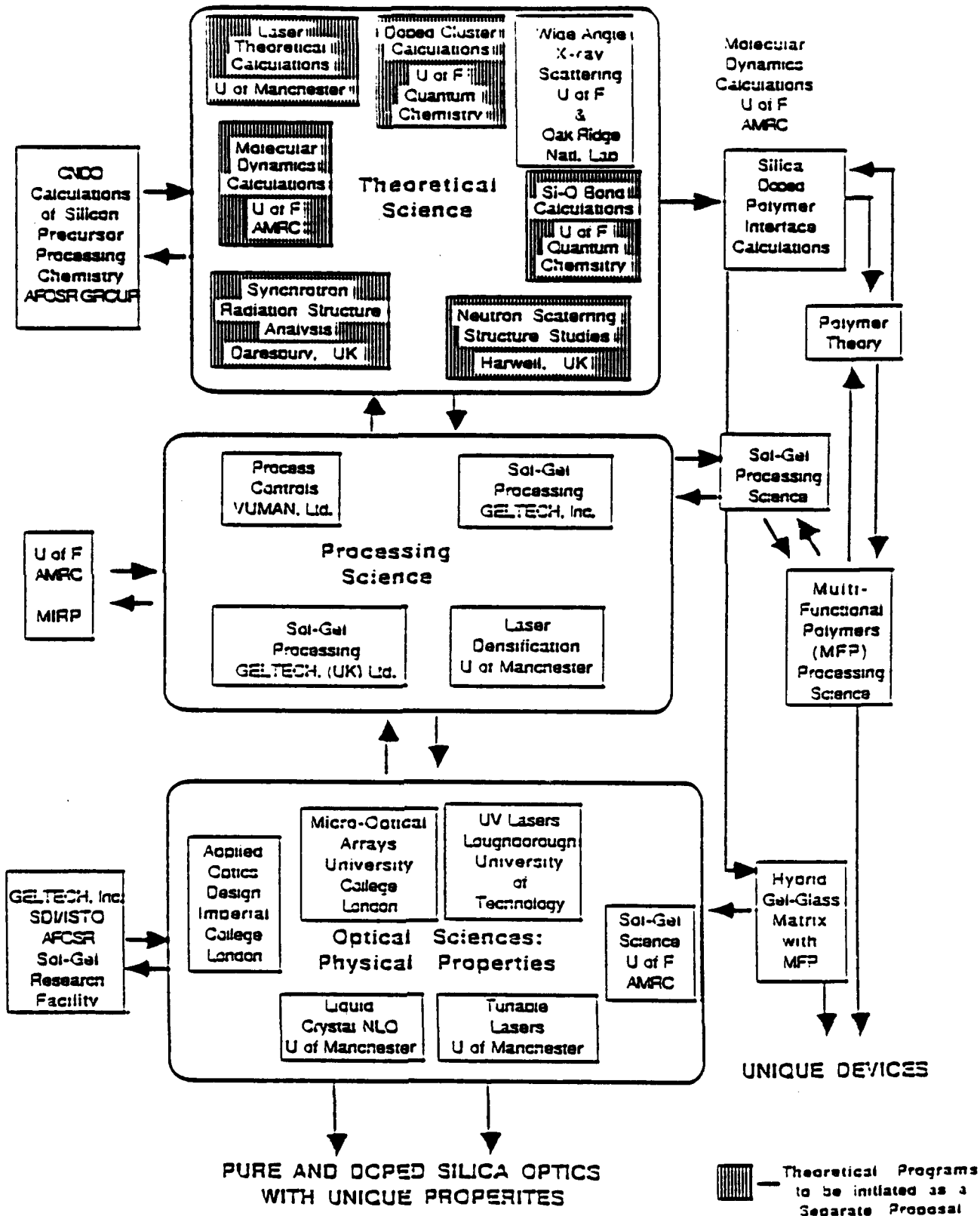


Figure 2

University College London). However, many other interactions continued and resulted in considerable progress in achieving multifunctional optical composites. A very broad range of characterization efforts were conducted to base the interactions on sound scientific understanding. Table 1 summarizes some of these efforts.

ACCOMPLISHMENTS

1) Optically transparent matrices with interconnected pores tailored to either 1.4 nm or 4.0 nm or 8.0 nm have been made by the University of Florida team (Figure 3) in the form of simple optical shapes of discs and rods. As-cast net shapes have been achieved. Excellent optical transmission in the ultraviolet at 250 nm has been obtained.

2) The surface chemistry of the matrices with 1.4 nm porosity has been characterized by the University of Brunel team (Figure 4). The surface hydroxyl content can be controlled by varying thermal treatments from 800 to 1000°C without collapse of the porosity or loss of optical quality.

3) A method for achieving uniform distribution of laser dye molecules within the 4.0 nm porous matrices has been developed by the University of Manchester team using impregnation processing of the gel-silica matrices (Figure 5). The wavelength range of organic doped gel-silica lasers has been extended by the University of Manchester team from the ultraviolet, 360 nm (using PBD dye) to 630 nm (using sulforhodamine 640 dye) using the 4.0 nm porosity gel-silica matrices (Figure 6A).

4) A 6X increase in quantum efficiency over solution operation of the same laser dye molecules has been achieved by the University of Manchester group for the organic laser dye contained within the gel-silica matrix.

5) Increased stability of the dye impregnated laser over ORMOSIL (method A) gel-dye lasers has been demonstrated by the University of Manchester team (Figure 6B).

6) Greater than 200 μm lifetimes of Nd^{3+} dopants in gel-silica matrices have been achieved by the University of Manchester team (Figure 7).

7) Stable laser densified spots have been produced on gel-silica substrates by the University of Manchester group (Figure 8).

8) In-situ polymerization of photopolymer in the 4.0 nm porosity gel-silica matrices has been achieved by the Loughborough University of Tech. team. The photopolymer/gel-silica matrix was illuminated by two coincident coherent beams from a 457.9 nm laser producing a 3-D grating with spacing controlled by the laser interference pattern (Figure 9). This successful proof-of-concept experiment opens the path for designing a new generation of distributed feed-back lasers and 3-D optical storage.

9) Technology transfer for this research program has been completed. Geltech, Inc., under license from the University of Florida, is now manufacturing porous Gelsil® matrices and selling them to many industrial firms and other University and U.S. Government laboratories.

Geltech, Inc. is producing commercial quantities of porous Gelsil® matrices for the continuation of Professor Terry King's development of multifunctional optical components, funded by private industry. A copy of Professor King's results presented at the International Sol-Gel Workshop in Paris, France in July 1993 is included as part of this Final report. Please note that this work presented was not funded in this program but is a result of the development effort that was supported financially by this program. Work leading to the paper "Spectroscopic Studies of Post Doped Silica Gel Monoliths" by C. C. Harrison and J. K. McGiveron also was not funded by this project. However, the samples were supplied by the project and previous spectroscopy studies reported by C. C. Harrison (previously C. C. Perry) and students were funded by the project.

Thus, this program has achieved its original goal of developing a new generation of optical materials which are now commercially available by a new United States manufacturing firm.

Table 1
Characterization Study

Characterization Test	Institution
TGA, DMA, DSC, DTA	UF
Dilatometry	UF
Microhardness	UF
Nitrogen Adsorption Isotherm Analysis	UF
Neutron Activation	UF
Index of Refraction	UF, Loughborough U. of Tech.
Optical Dispersion	Subcontract
Surface Finish and Figure	UF
Dimensional Tolerance	UF, Loughborough U. of Tech.
Homogeneity (Zygo Interferometer)	UF
FTIR	UF, Brunel University
UV, VIS, NIR	UF, Brunel University
Vacuum UV	UF, Subcontract
AFM	Digital Instrument
Raman Spectroscopy	UF, Brunel University
Inorganic Doping	Brunel University, UF
Organic Doping	University of Manchester University of Buffalo Loughborough U. of Tech., UF
Positronium Decay	TCU
Neutron Scattering	University of Reading
Synchrotron Scattering	University of Montpellier
X-ray Small Angle Scattering	University of Sao Paolo
Pressure IR	University of Illinois
Vapor Stabilization	University of Wisconsin
Gas Permeability	UF
Liquid Diffusivities	UF
AC Impedance Spectroscopy	UF

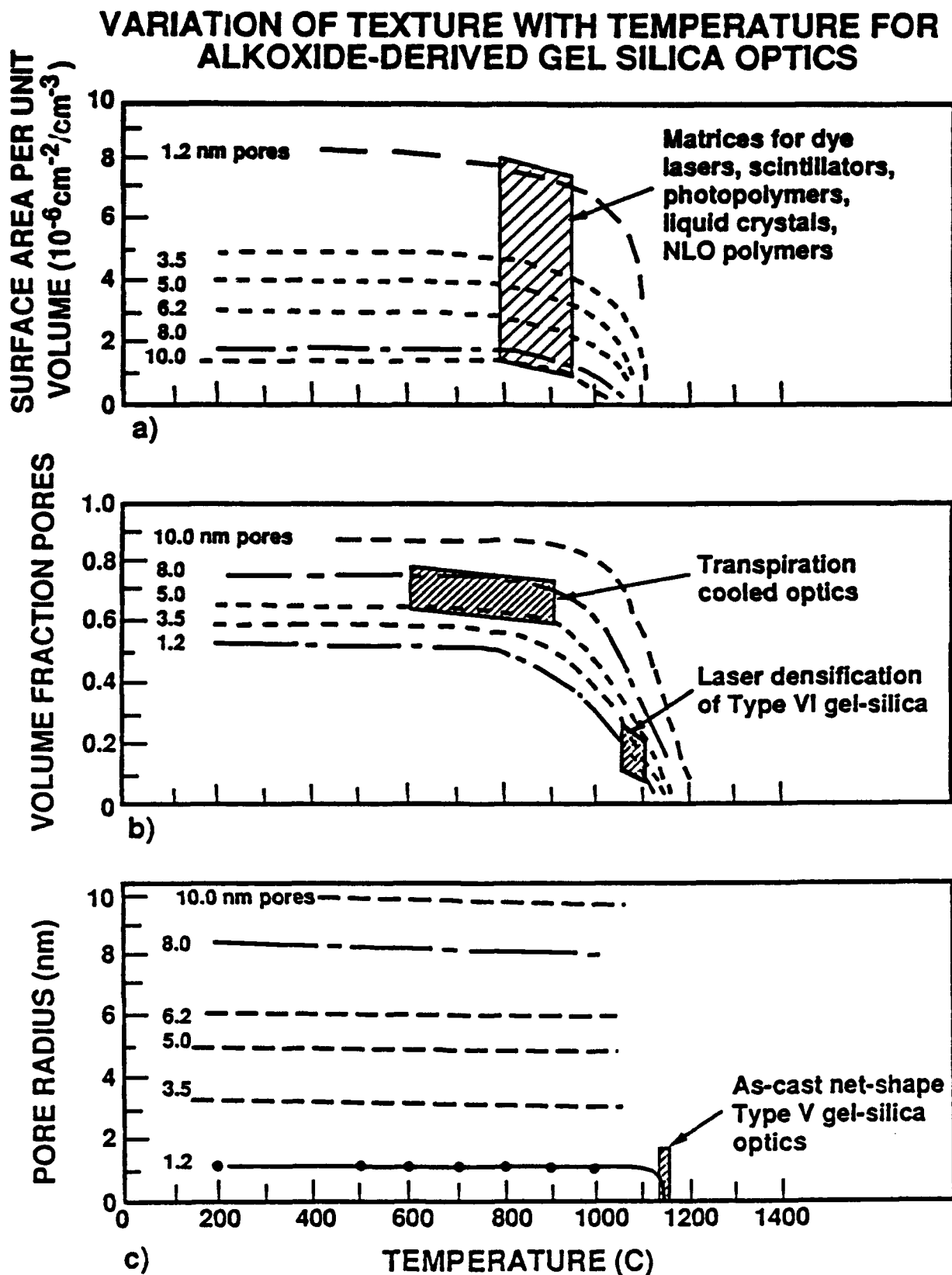


Figure 3

STRUCTURAL STUDIES OF SOL-GEL DERIVED GELS AND GLASSES

Carole C. (Perry) Harrison

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Uxbridge
Middlesex
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OBJECTIVES

To relate sol-gel microscopic structural chemistry to the sol-gel process. To investigate the effects of bulk and surface structure on the incorporation of inorganic and organic moieties within porous gel-glasses.

ACCOMPLISHMENTS

The development of structural models for the bulk and surface structure of thermally treated silica and silica/titania gel glasses. The application of these models to understanding the fate of metal ions (Co^{2+} , No^{3+}) and dye molecules (Rhodamine 6G) on incorporation into a variety of porous gel-glasses.

APPROACH

Microscopic and spectroscopic studies of monolithic materials and powders. A range of techniques are used including

- Electron microscopy
- Infrared spectroscopy
- FT-Raman spectroscopy
- Near infrared spectroscopy
- UV/Vis spectroscopy
- Solid state nmr
- EXAFS
- Gas adsorption
- Small angle scattering

Near infrared spectra showing changes in silica surface functionalities with increasing hydration.

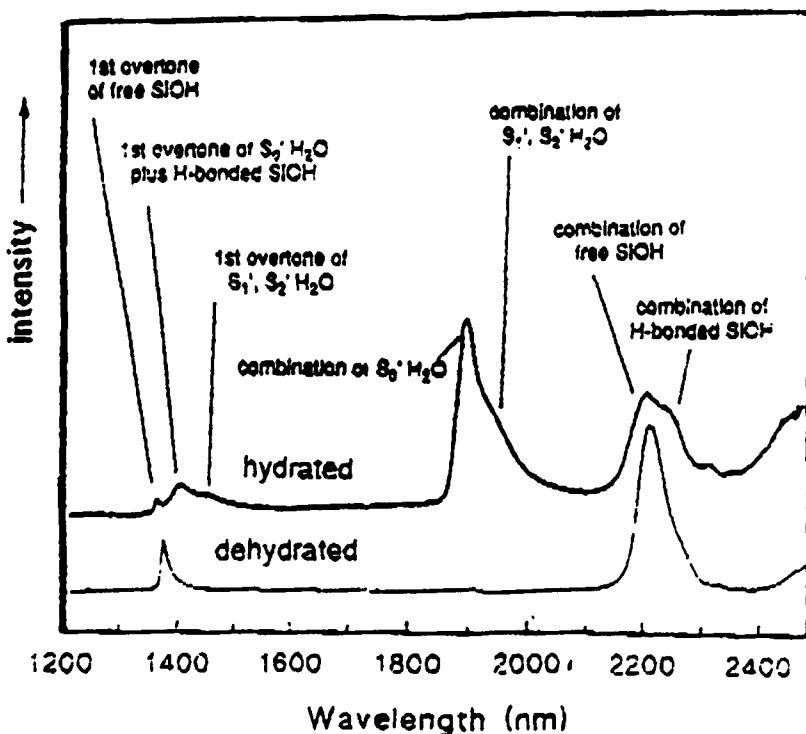


Figure 4

OPTICAL COMPOSITES PROCESSING

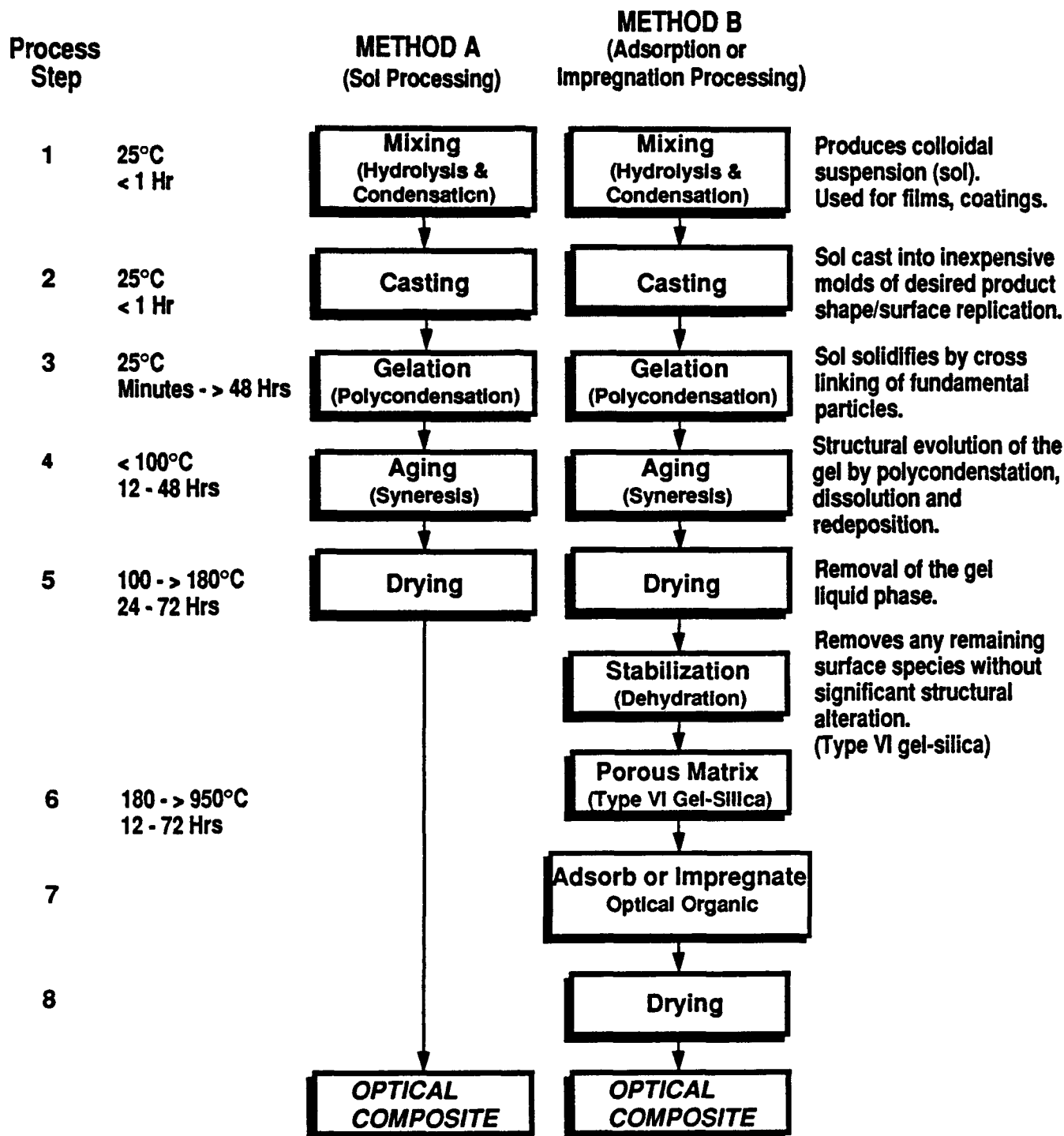


Figure 5

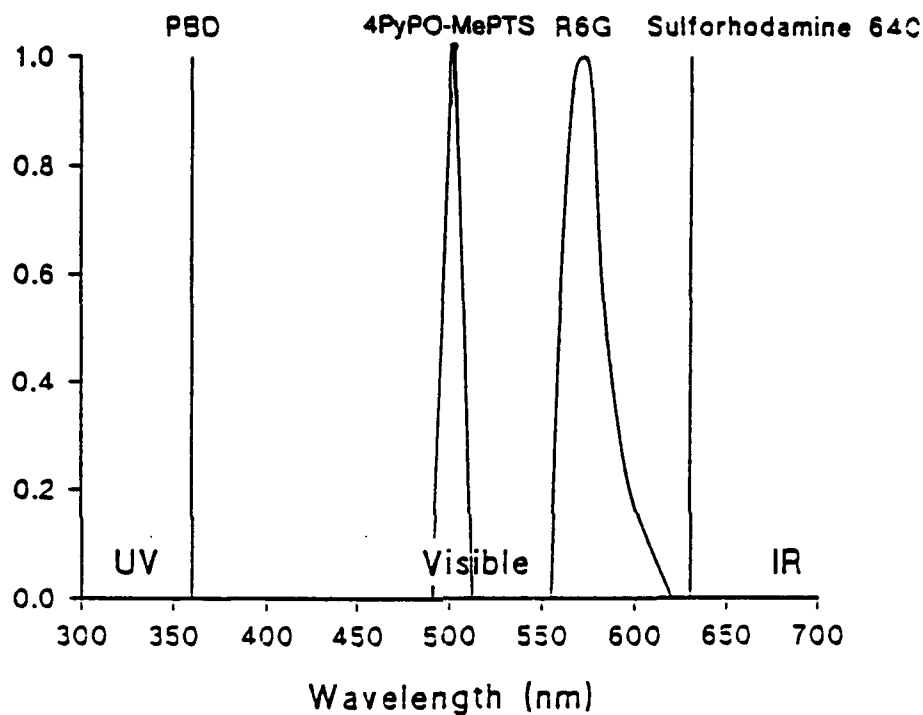
SOLID STATE TUNABLE DYE LASERS

BY IMPREGNATION OF LASER DYES

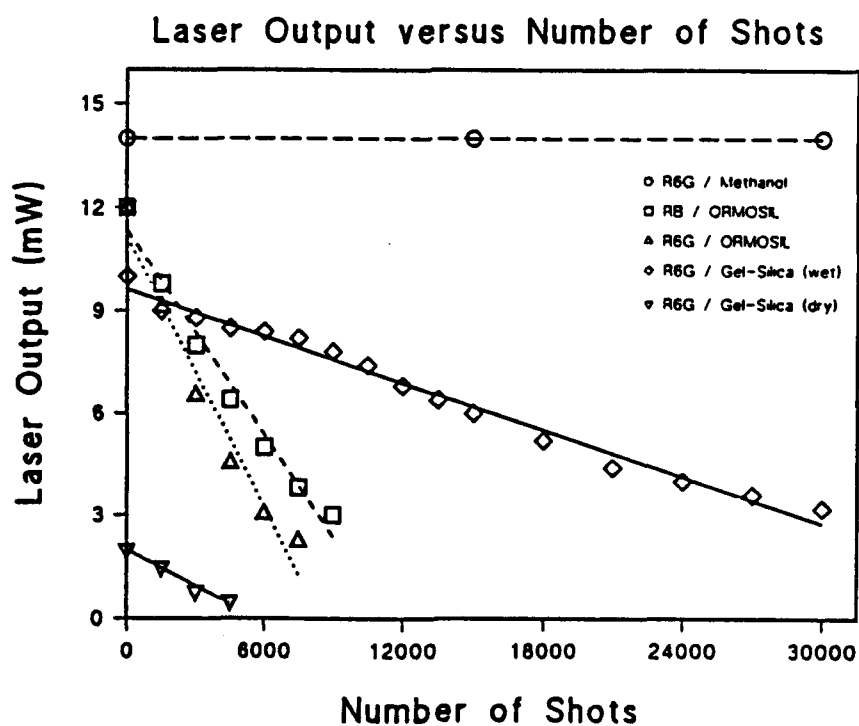
IN

POROUS TYPE VI GEL-SILICA MATRICES

developed by
T. King (U. Manchester) and L.L. Hench (U. Florida)



(A)



(B)

Figure 6

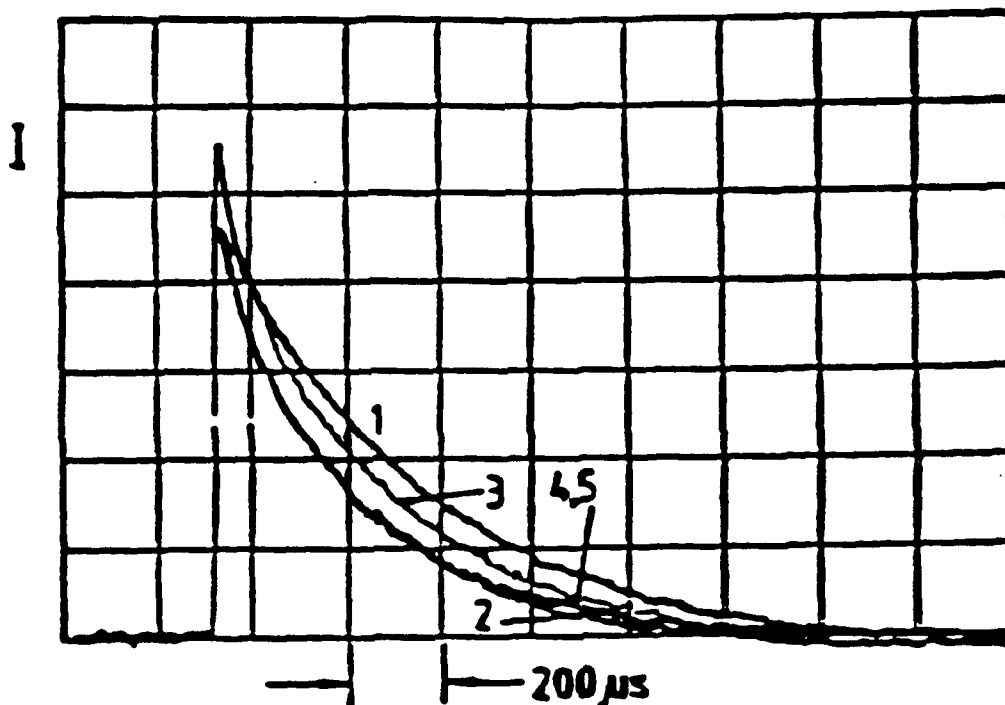


Figure 5.
Lifetimes of Nd^{3+} in laser glass (1,2) and in sol-gel glass (3,4,5)

LASER DEVELOPMENTS IN SOL-GEL GLASS

D.Shaw, C.Whitehurst, A.Charlton and T.A.King.

Physics Department

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Manchester

England

M13 9PL.

LASER DENSIFICATION OF OPTICAL ELEMENTS IN GEL-SILICA MATRIX

T. King and D. Shaw • University of Manchester, U.K.
and

L.L. Hench and J.K. West • University of Florida

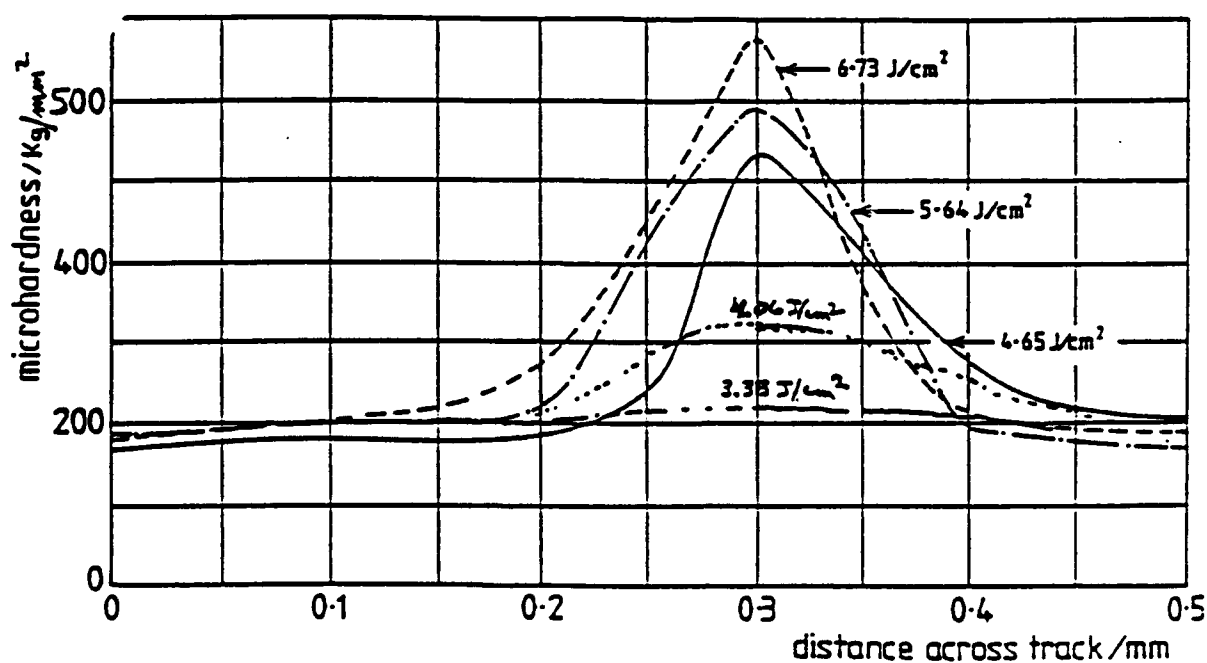
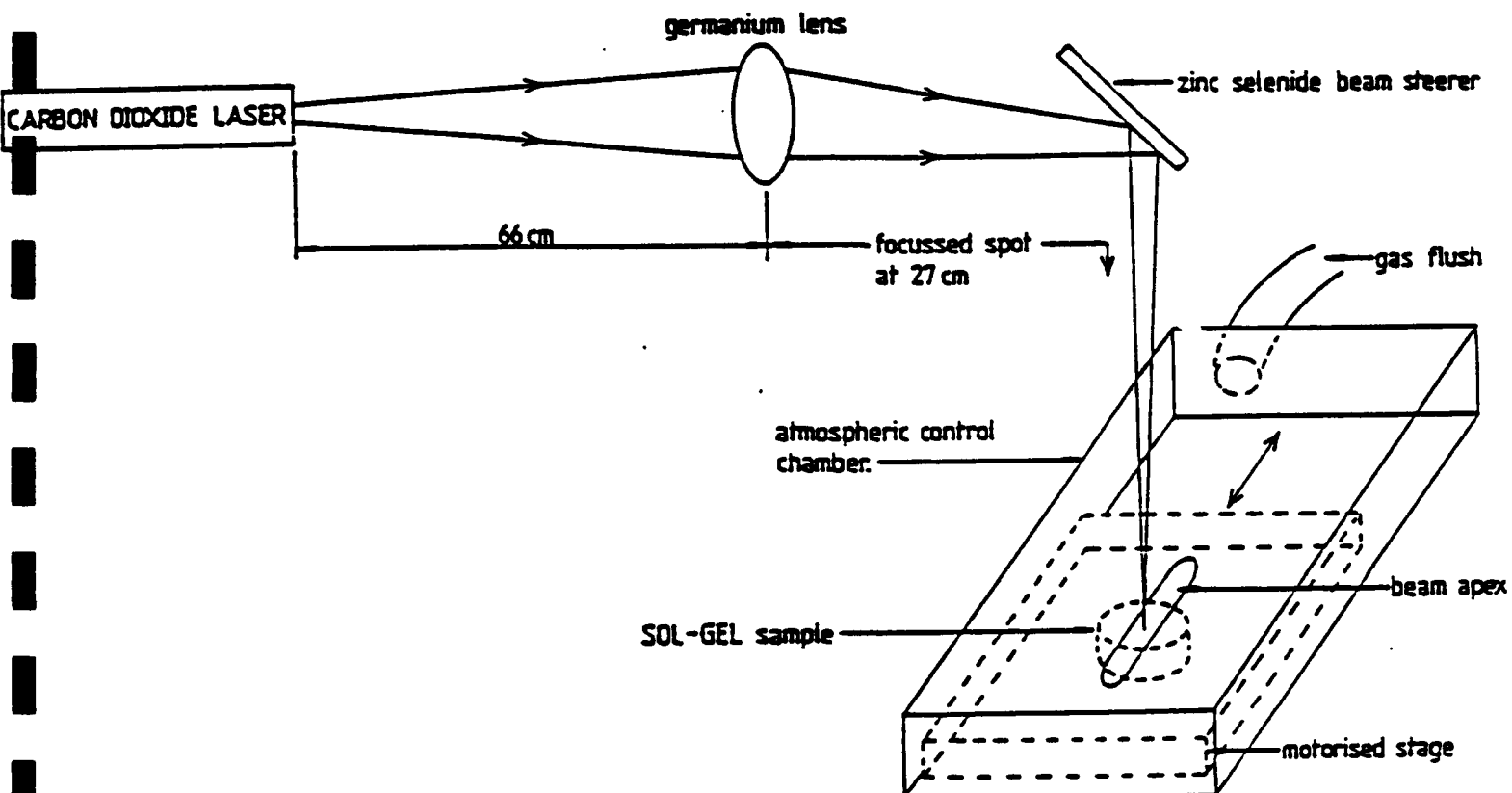


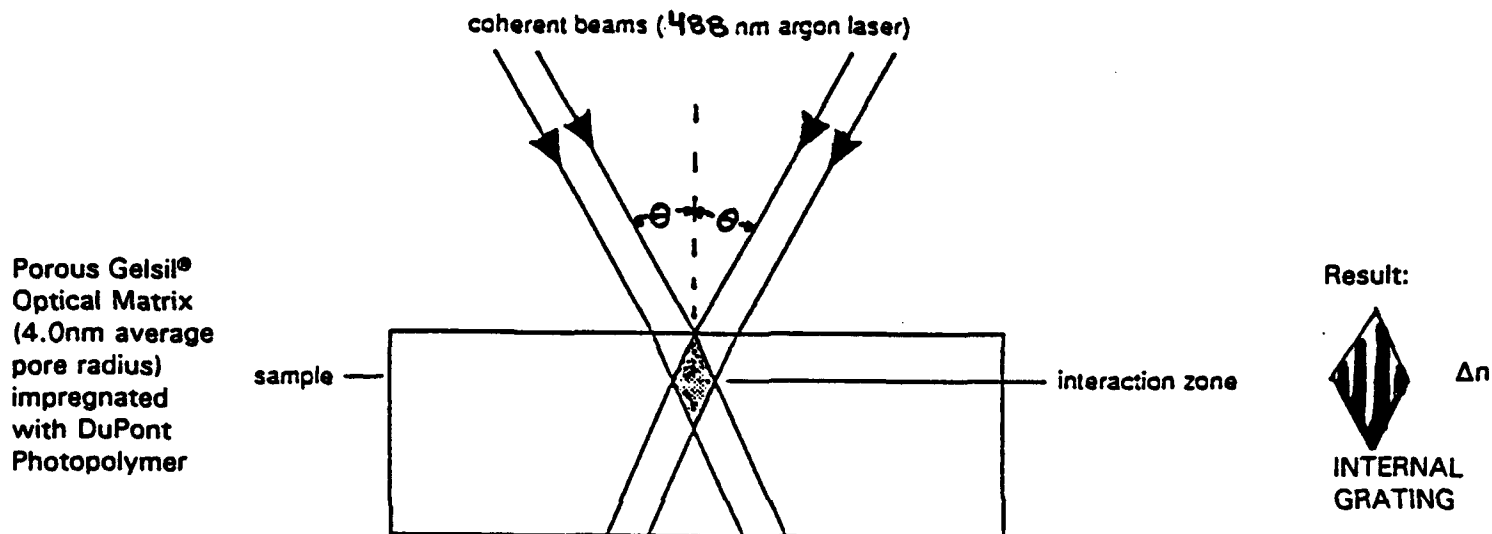
Figure 8

INTERNAL OPTICAL GRATINGS

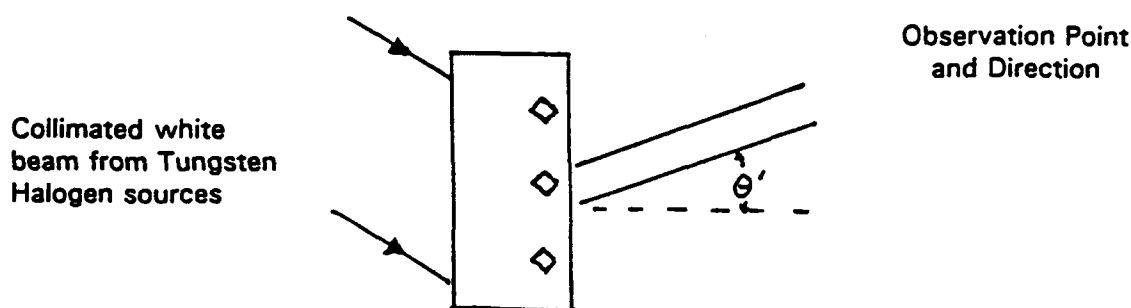
Nick Phillips (Loughborough University of Technology)
Larry Hench (University of Florida, AMRC)

Objective: Use Porous Gelsil® Optical Matrices impregnated with DuPont Photopolymer to produce internal optical gratings.

Method of Recording the Grating:



Method of Replay:



Features:

- By changing angle of observation θ' then color changes.
- Colors are intense because of frequency selectivity of a thick grating.
- Spot size is set by laser beam diameter.
- Boundary of spot is as sharp as beam boundary.
- Very thick gratings should permit extreme angular selectivity e.g., as in lithium niobate crystals. Can illuminate with more than one beam simultaneously.

Figure 9

SECTION II

SOL-GEL SILICA

a. Gel-Silica Optics: Theory and Application

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ABSTRACT

A new generation of silica optics has resulted from alkoxide-based so-gel processing of silica including: net shape transmissive optical elements, surface diffractive optics, inorganic doped GRIN optics, organic impregnated optical composites such as dye lasers and scintillators, optics with internal diffraction gratings, laser densified microoptical lenses and arrays, and laser densified waveguides. Processing control of the ultrastructure of the monolith at the time of gelation and during aging is essential to producing the optical devices together with chemical and thermal stabilization of the surface of the pore network prior to densification or impregnation. The process control variables for gel-silica optics are summarized together with spectroscopic analysis and molecular orbital calculations that explain how and why the thermal-chemical processing controls work at a molecular level.

INTRODUCTION

Hench, Wang and Nogues¹ reported on a method using alkoxide based sol-gel processing to produce two new types of optical silicas. Type V gel-silica optics, following Bruckner's notation,² is a full density amorphous silica. It has excellent optical properties equivalent to or superior to other commercial optical silicas, Types I-IV. A Type V gel-silica has excellent ultraviolet, visible and near infrared transmission qualities. It also has high homogeneity, very low strain birefringence and a lower coefficient of thermal expansion than other silicas.³ An important advantage of Type V gel-silica optics is the ability to cast a sol at ambient temperature into precision molds made of inexpensive polymers. Thus, net shape and net surface optical components can be produced rapidly

without time consuming and expensive grinding and polishing. Surface diffractive features can be replicated in the silica optics through the casting process as well.

The second new type of optical silica is termed Type VI.¹ The Type VI gel-silica glass has a residual porosity which is sufficiently small to avoid extensive light scattering in the visible. The porous gel-silica matrix can be used as a substrate for laser writing of micro-optical arrays and waveguides, as reported by Chia and Hench.⁴ The chemical stability of the porous gel-silica network makes it possible to impregnate into the Type VI gel-silica a wide range of optically active compounds, including laser dyes, scintillators, and wavelength shifters.^{1,5,6} Impregnation of Type VI gel-silica optical matrices provides one alternative to the production of optical composites.⁷ The other alternative to optical composite processing involves mixing the polymer phase and the inorganic silica phase together prior to gelation. Studies by Reisfeld, Avnir and colleagues in Israel,⁸⁻¹⁰ Mackenzie¹¹ and Dunn^{12,13} and co-workers at UCLA, Prasad and Karasz¹⁴ at Buffalo and University of Massachusetts have shown the unique features of optical composites made by combining inorganic and organic phases.

Previous work from our group^{1,5,7} and also from Nogues and co-investigators,⁶ King and co-workers^{15,16} at the University of Manchester, UK and Phillips and colleagues¹⁷ at Loughborough University of Technology in the UK, have shown the merit of using Type VI gel-silica matrices as a route to producing optical composites. However, most of the early work from Florida, Manchester and Loughborough has emphasized the use of Type VI gel-silica optical matrices with very small pores of 1.2 to 1.4 nm radius. For a number of applications, however, pores this small are difficult to impregnate with larger molecular weight organic species. The small pores also make it difficult to obtain a homogeneous distribution of the organic phase, in some cases.¹⁶ Consequently, the goal of this work is to achieve a reliable means of producing gel-silica matrices with larger pore sizes. Previous work has shown that both 4.0 nm radius pore matrices and 9.0 nm

matrices are feasible.^{18,19} This paper reports the textural characteristics and the properties of matrices made in large enough quantities to obtain statistical variability and the results from newly made 3.2 nm radius porous matrices. Results are compared with previous work²⁰ that describe the texture and properties of a 1.4 nm porous matrices made commercially by Geltech, Inc.

EXPERIMENTAL PROCEDURE

The method for producing the large pore matrices is based on the catalysis of a silicon alkoxide precursor, TMOS, with a mixture of dilute nitric and hydrofluoric acids¹⁹. The pore radii of matrices made by the HF and HNO₃ method can be engineered to be between 3.2 and 5.0 nm. In contrast an ammonia aging process described by Liu and Hench²¹ yields matrices with approximately 9.0 nm radius pores. These alternative processes yield monolithic structures with high reliability of >80% yield and reproducible dimensions and textures. The larger pore matrices provide a useful alternative to the previously described 1.2 and 1.4 nm pore radius matrices made using the sol-gel process with nitric acid catalysis of the tetramethyl orthosilicate alkoxide precursor.^{1,3}

Figure 1 summarizes the HF and ammonia based processing for the sol-gel matrices. There are six steps in the process that lead to a chemically and thermally stable optically transparent gel-silica matrix. Processing of the matrices is followed by vacuum adsorption or impregnation of the second phase optical organic. Finally, residual carrier liquid used in impregnation is removed by low temperature drying which does not harm the organic phase. This is one of the primary advantages of this method of making optical composites. Details of the HF and ammonia process follow.

To prepare the 30 Å and 45 Å Type VI gel-silica samples for this study high purity (99.9% pure) tetramethoxysilane (TMOS) was mixed with a dilute solution of high purity deionized water

and reagent grade nitric and hydrofluoric acid and allowed to stir rapidly for several minutes to allow complete hydrolysis of the TMOS. The sol was filtered and cast into Teflon molds which had been cleaned, dried and blown free of all dust. The casting process was completed within several minutes prior to gelation, which occurs very rapidly for this system, Fig. 1. The molds were placed onto a level surface to insure that all samples have parallel surfaces. The samples were held at room temperature for 48 hrs. before aging above 100°C. After aging, the samples were transferred into drying chambers which were placed in a 125°C drying oven and allowed to oven cool to room temperature. The samples were then placed into quartz crucibles and stabilized in ambient air at a stabilization temperature of 700°C-1150°C. After stabilization all samples were labeled and stored in desiccators before being analyzed.

The process used to produce the matrices with 90 Å pores was similar to that described above with the major exception being a 24 hr. aging treatment in a dilute NH_4OH solution prior to drying (Fig. 1).

CHARACTERIZATION OF PORE NETWORKS

Nitrogen adsorption isotherm analysis was used to determine the texture of the gel-silica pore matrices. An Autosorb 6 nitrogen absorption/desorption system (Quantachrome Corporation) was used for analyzing the matrices. The samples were cast as either 2 cm diameter disks or squares. The thicknesses were approximately .5 cm. All samples were dried in a vacuum oven at 120°C for 24 hours before analysis, following previously reported techniques.²¹ For N_2 adsorption isotherm analysis the samples were ground into powders with a mortar and pestle and out-gassed at 120°C under vacuum until no further weight changes were observed. Typical absorption/desorption isotherms for the 30 Å, 45 Å and 90 Å samples, stabilized at 1000°C in air for 1 hour, are compared in Fig. 2 with the isotherm for the 12 Å gel matrices, which is virtually the

same as the 14 Å sample. There is a substantial difference in the shape of the adsorption isotherms. The significance of these differences is due to the shape of the pore necks, as discussed by Liu and Hench.²¹ The pore size distribution for the four types of gel-silica matrices are compared in Fig. 3. The distribution is narrow for all four types of matrices, and is especially narrow for the 30 Å matrices. The average size of the porosity, calculated from the size distribution curves, was 14 Å, 30 Å, 45 Å, and 90 Å. The textural characteristics of five to seven samples were analyzed for each stabilization treatment with the average and ± 1 standard deviation shown in Figs. 4-7. (The size of the data points represents ± 1 standard deviation from the mean.) The curves in Figs. 2 and 3 are representative of the samples with average values of the textural characteristics. Results from Fig. 3 show that there is a relatively small tail of pore sizes larger than the average pore radius. Consequently, there is relatively little Raleigh scattering due to the porosity, even with pore radii up to 90 Å.²²

EFFECT OF TEMPERATURE ON PORE CHARACTERISTICS

One of the most important variables in controlling the texture of the gel-silica matrices is the stabilization temperature. Previous studies^{19,20} showed that the 12 and 14 Å porous matrices did not change pore size with thermal treatments from 700 to 1000°C. These results are compared in Fig. 4 with the larger pore matrix materials reported here. There is an advantage in stabilizing at as high a temperature as possible, consistent with maintaining a large volume of open porosity. The reason is the improved chemical and thermal stability of gel-derived silicas with the elimination of surface silanols and three membered silica rings²³⁻²⁶ at temperatures in excess of 700-800°C. Consequently, the textures of 30 Å, 45 Å and 90 Å porous matrices were investigated over a temperature range from 900-1150°C. The results are highly consistent with very little variation over a set of 5 to 7 samples for each stabilization temperature.

The average pore size of the 30 Å matrices remains stable up to 900°C, with a decrease to 20 Å during a 1000°C thermal treatment. There is very little change in the pore size of the 45 Å matrices from 900-1050°C. A small decrease occurs between 1050 and 1100°C. The 90 Å matrices show very little change in average pore size up to temperatures of 1150°C.

Although pore size is stable during stabilization treatments from 800-1000°C, sintering is occurring. Figure 5 compares the surface area, m²/g, of the small pore (12 Å and 14 Å) matrices with the 30 Å, 45 Å and 90 Å matrices. The 12 Å and 14 Å gel-silicas initially have surface areas in the range of 600 to 700 m²/g. These very large surface areas begin to decrease at 800°C and substantial sintering has occurred by 1000°C. The commercial Geltech materials, with 14 Å porosity, are more stable up to 1000°C than the experimental University of Florida materials with 12 Å pores investigated by Vasconcelos.^{18,27} The matrices with 30 Å pore radius have a surface area of 550 m²/g up to 800°C. It decreases to 450 m²/g at 900°C and 200 m²/g at 1000°C. The matrices with 45 Å porosity have a surface area in the range of 350 m²/g at 900°C which decreases uniformly to a value of 250 m²/g at 1100°C. The matrices with 90 Å pores have surface areas after a 1000°C treatment of approximately 230 m²/g which remains relatively unchanged to 1150°C.

The thermal stability of the 30 Å, 45 Å and 90 Å porous matrices is important because it makes it possible to maintain a large interconnected pore volume and also achieve a low concentration of surface silanols and trisiloxane rings which are metastable to hydration. The effect of stabilization temperature on pore volume is shown in Fig. 6. The small pore matrices have pore volumes in the range of 0.4 to 0.5 cc/g below 800°C decreasing to only 0.3 at 1000°C for the commercial, 14 Å matrices. In contrast, the matrices with 30 Å and 45 Å pores have much larger pore volumes in the range of 0.8 to 0.9 cc/g for the 30 Å and 45 Å matrices below 800°C. The pore volume for the 45 Å matrices decreases to about 0.6 cc/g at 1000°C while the pore volume of the

30 Å matrices is approximately 0.2 cc/g at the same temperature. The large change in pore volume for the 30 Å matrices can be attributed to a much slower heating rate above 800°C than used for the 45 Å or 90 Å matrices. The 30 Å samples were developed for laser densification and waveguide production which requires higher bulk densities than matrices used for impregnation. These results demonstrate the importance of the thermal schedule in the production of porous matrices for a variety of different applications. Figure 6 shows that the pore volume decreases continuously over the stabilization temperature range. However, even after the 1100°C treatment there is still 0.6 cc/g of porosity remaining in the 45 Å matrix. The 90 Å material has an even larger pore volume of 1.0 cc/g at 1000°C and even after a 1150°C stabilization treatment it still has 0.9 cc/g of interconnected open porosity.

PHYSICAL PROPERTIES

The bulk density of the matrices was obtained by two different experimental methods. The data in Fig. 7 are from mercury pycnometry measurements which compare favorably with bulk density values obtained by measuring the geometric dimensions of the as-cast cylindrical specimens. The relative volume fraction of porosity, based upon full density of 2.2 g/cc, is indicated by the scale on the right side of Fig. 7.

Densification begins to occur at 800°C for the matrices with 12 and 14 Å porosity. The smaller pore materials have increased to bulk densities of 1.7 g/cc at 1000°C. This corresponds to 77% of full density vitreous silica (2.2g/cc). The matrices with 14 Å porosity have an increased bulk density of 1.35 g/cc, 61% full density after 1000°C stabilization. One of the restrictions of the use of the very small pore materials is the reduced volume of porosity when the materials are heated to sufficient temperature to achieve maximum thermal and chemical stability. The 39%-23% residual porosity is interconnected and small molecules can be adsorbed into the network by vacuum

impregnation but it is difficult to obtain homogeneous distribution of a second phase in the restricted channels (see Fig. 2 isotherm).

The matrices with 30 Å and 45 Å porosity have bulk densities as low as 0.75 g/cc, which corresponds to 0.6 to 0.5 volume fraction of porosity, at 900°C. Even after 1100°C stabilization the bulk density of the 45 Å matrices has increased to only 0.95 g/cc, which is 45% of full density vitreous-silica. Thus, the volume percentage of porosity for the matrices with 45 Å pores can be varied from 0.65 volume fraction of pores to 0.55 volume fraction of pores with stabilization temperatures over the range of 900 to 1100°C.

The matrices with 90 Å pores have even lower bulk densities, 0.66 g/cc at 1000°C. There is little sintering and densification even up to 1150°C with the bulk density increasing only to 0.72 g/cc. Thus, the matrices with 90 Å have between 0.65 to 0.6 volume fraction of residual porosity available for impregnation with second phases, such as optically active organic molecules.

The large volume fraction of porosity in the 30 Å, 45 Å and 90 Å matrices has a marked effect on the mechanical properties of the material, as first described by Vasconcelos and Hench²⁷ on preliminary studies of this type of optical matrix. Figure 8 shows the Knoop hardness of the matrices as a function of stabilization temperature. The Knoop indentation load was 200 g. The Knoop indenter produces a more accurate hardness measurement for these mechanically fragile matrices than the Vickers hardness indenter used by Vasconcelos.^{18,27} The statistical variability of the results are indicated by the size of the data points which show ± 1 standard deviation from the average hardness value. The hardness of the 30 Å and 45 Å material increases by over three times for stabilization treatments at 1100°C. The 30 Å and 45 Å materials therefore are much more attractive for use as an optical element because of their ability to be polished and their resistance to abrasion. The 90 Å matrices have 4 times lower hardness, of only 10 Knoop hardness units after

a 1000°C heat treatment. Heating up to 1150°C does increase the hardness to 15, however, these are relatively fragile materials.

Thus, there is a trade off between the large volume percent of porosity available for the 90 Å matrices vs their relatively poor mechanical properties. In contrast, the matrices with 30 Å and 45 Å porosity have a desirable combination of residual porosity ranging from 65 to 55 volume % with good mechanical properties.

OPTICAL TRANSMISSION

Matrices with 14 Å, 30 Å, 45 Å, or 90 Å pores are transparent in the visible, as illustrated in Fig. 9. There is almost no scattering by the 14 Å samples, very little for the 45 Å, but a small amount of scattering is apparent for the 90 Å matrix.

The effect of pore size on transmission in the UV is shown in Fig. 10. Full density Type V gel-silica has almost no absorption out to 185 nm. (Note: Transmission shows < 100% due to surface scattering since the measurements were made on samples with as-cast surfaces from unpolished molds.) The commercial sample with 14 Å pores has a 1% UV cut-off at 193 nm (Table 1) and 50% transmission at 301 nm. The matrix with 30 Å and 45 Å pores has less transmission in the UV with a 1% UV cut-off at 255 nm and 304 nm; respectively; the matrix with 90 Å pore size has a 1% cut-off at 343 nm. All four types of Type VI gel-silica samples were stabilized at 1000°C in air.

The decrease in transmission shown in Fig. 10 is due to Raleigh scattering, according to calculations by West and Elias²². However, Phillips and King have shown that if an index matching organic is impregnated into these matrices and polymerized in-situ the scattering is eliminated²⁸.

APPLICATIONS: ONE-TO-FOUR GEL-SILICA WAVEGUIDES

Previous studies have shown the use of the Type VI porous gel-silica matrices as a host for organic scintillators⁶, wavelength shifters,^{5,7} and laser dyes,^{12,16,29} and photopolymerized internal diffraction gratings.¹⁷ Application of porous gel-silica matrices for transpiration cooled optics has also been demonstrated.³⁰ Recently, Type VI gel-silica matrices have been used as substrate for laser densification of microoptical arrays and waveguides.^{4,31}

Passive optical waveguiding devices play an important role in optical signal processing. Optical power dividers are key components in subscriber and in local area networks of optical fiber communications to divide an optical signal into two or more branches. Subscriber networks require long distance data transmission, for which single mode step index optical fibers are the more suitable media, due to the large bandwidth they provide compared to multimode fibers. Opposing that, multimode transmission is now being proposed for local area networks, because multimode fiber-to-waveguide coupling does not require very precise alignment, a difficult process when dealing with single mode devices.

The production of one-to-four branching waveguides comprises basically all the steps in the production of any optical power divider, the number of output branches depending on the requisites of the particular system where the device will be used. One-to-four power dividers are common devices in single mode optical communications, with branches with a width of around 4 μm . Multimode optical communications makes use of $N \times N$ star couplers, with branches with widths varying from 50 to 100 μm . Laser densification makes it possible to produce any of these configurations with only small variations in processing variable.

The one-to-four optical waveguides produced by the AMRC (see Fig. 11) have branches with widths around 400 μm , obtained by densification of type VI gel-silica 30 Å substrates with a CO_2

laser. Use of the 30 Å matrices and new laser process controls described elsewhere in this conference make it possible to produce waveguides of 50 μm width.³²

CONCLUSIONS

Sol-gel processing of silica can be controlled to produce porous optical matrices with average pore sizes of 14 Å, 30 Å, 45 Å, and 90 Å and narrow pore size distributions. The porosity is interconnected and can be vacuum impregnated with an optically active second phase. These larger pores allow the matrix to be molecularly tailored at a nanometer scale for specific inorganic and organic molecules. The volume percent of porosity in the matrices is a function of pore size and stabilization temperature, i.e., 14 Å matrices have 39-48% porosity, 30 Å matrices have 50-60%, 45 Å matrices have 55-68% porosity, and 90 Å matrices have 68-70% porosity. This range of textures makes it possible to select a matrix to match organic phases with specific molecular weights. Variation in stabilization temperature can be used to optimize the pore surface chemistry to match the impregnated phase. The porous matrices can also be densified locally with a CO₂ laser to make microoptical arrays, waveguides, and dividers. Optical composites made in this manner are mechanically tough and chemically stable since the matrices have been thermally stabilized from 900-1150°C prior to incorporation of the organic phase or irradiated.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of the Air Force Office of Scientific Research (AFOSR) under contract number F49620-88-C-0073 for this work.

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Table 1
Effect of Pore Size on UV Transmission of Type VI
Gel-Silica Optical Matrices

Type VI Gel-Silica (1000°C)	12 Å Pores	30 Å Pores	45 Å Pores	90 Å Pores
50% UV Transmission	320 nm	346 nm	480 nm	538 nm
1% UV Cut-Off	195 nm	221 nm	313 nm	346 nm

FIGURE CAPTIONS

- Fig. 1. Processing of porous gel-silica optical matrices
- Fig. 2. N_2 adsorption/desorption isotherms for Type VI gel-silica matrices with different average pore radii.
- Fig. 3. Pore size distributions for Type VI gel-silica matrices with different average pore radii.
- Fig. 4. Average pore radius vs. process temperature for 12 Å, 14 Å, 30 Å, 45 Å and 90 Å Type VI gel-silica.
- Fig. 5. Surface area vs. process temperature for 12 Å, 14 Å, 30 Å, 45 Å and 90 Å Type VI gel-silica.
- Fig. 6. Pore volume vs. process temperature for 12 Å, 14 Å, 30 Å, 45 Å and 90 Å Type VI gel-silica.
- Fig. 7. Bulk density vs. process temperature for 12 Å, 14 Å, 30 Å, 45 Å and 90 Å Type VI gel-silica. The percentage of density relative to vitreous silica ($\rho = 2.2$ g/cc) is shown.
- Fig. 8. Knoop hardness vs. process temperature for 30 Å, 45 Å, and 90 Å Type VI gel-silica.
- Fig. 9. Transparency in the visible of Type VI porous gel-silica optical matrices for 14 Å, 30 Å, 45 Å, and 90 Å.
- Fig. 10. Ultraviolet transmission of Type V full density gel-silica and Type VI porous gel-silica matrices with 14 Å, 30 Å, 45 Å, and 90 Å average pore radii.
- Fig. 11. One to Four laser written waveguided on sol-gel type VI silica.

Time and Temp. for HF Process	Time and Temp. for NH ₄ OH Process	Process Steps
H ₂ O/TMOS = 16 (HF + HNO ₃) 25°C 7 min.	H ₂ O/TMOS = 16 HNO ₃ 25°C 40 min.	(1) Mixing (Hydrolysis & Condensation)
25°C, 5 min.	25°C, 15 min.	(2) Casting
25°C, 1 min.	40°C, 48 hrs.	(3) Gelation (Polycondensation)
> 100°C in pore liquor 48 hrs.	In 80°C NH ₄ OH Sol'n 1 day	(4) Aging (Syneresis)
125°C 36 hrs.	180°C 68 hrs.	(5) Drying
900°C - 1100°C 1 hr. or more	1000°C - 1150°C 1 hr.	(6) Stabilization (Dehydration)

Fig. 1

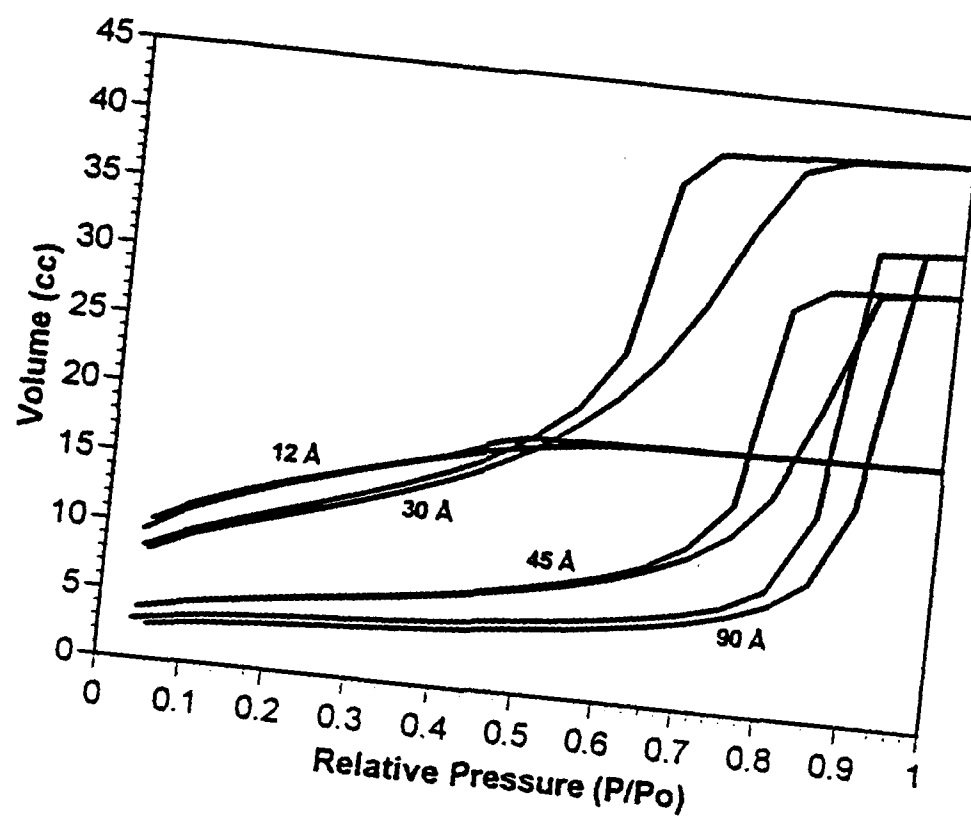


Fig. 2

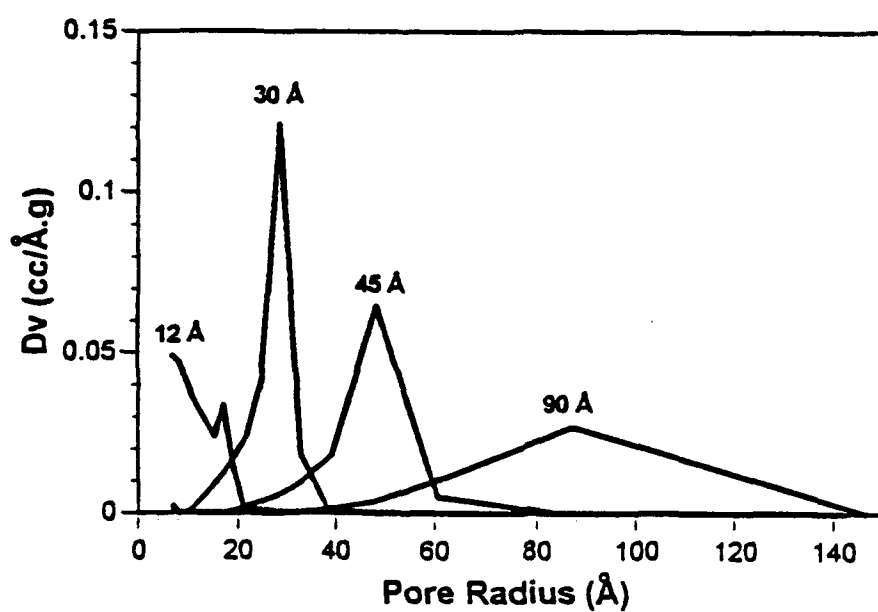


Fig. 3

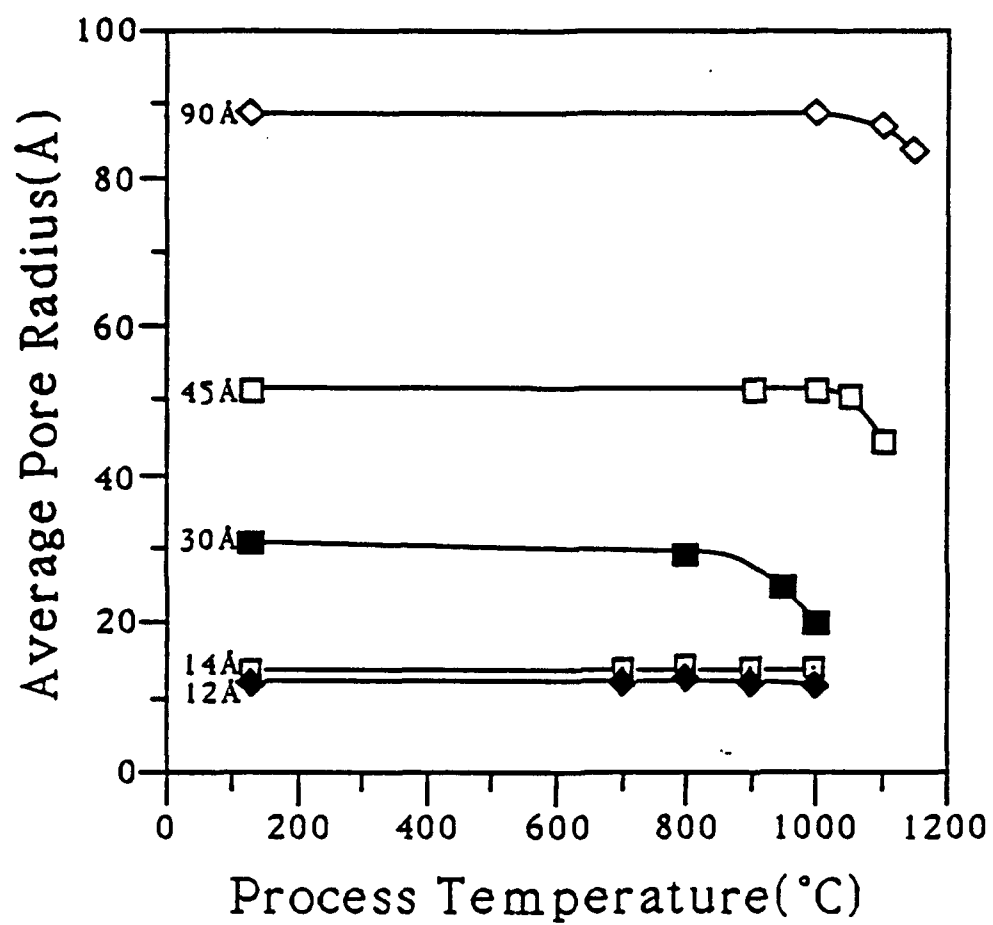


Fig. 4

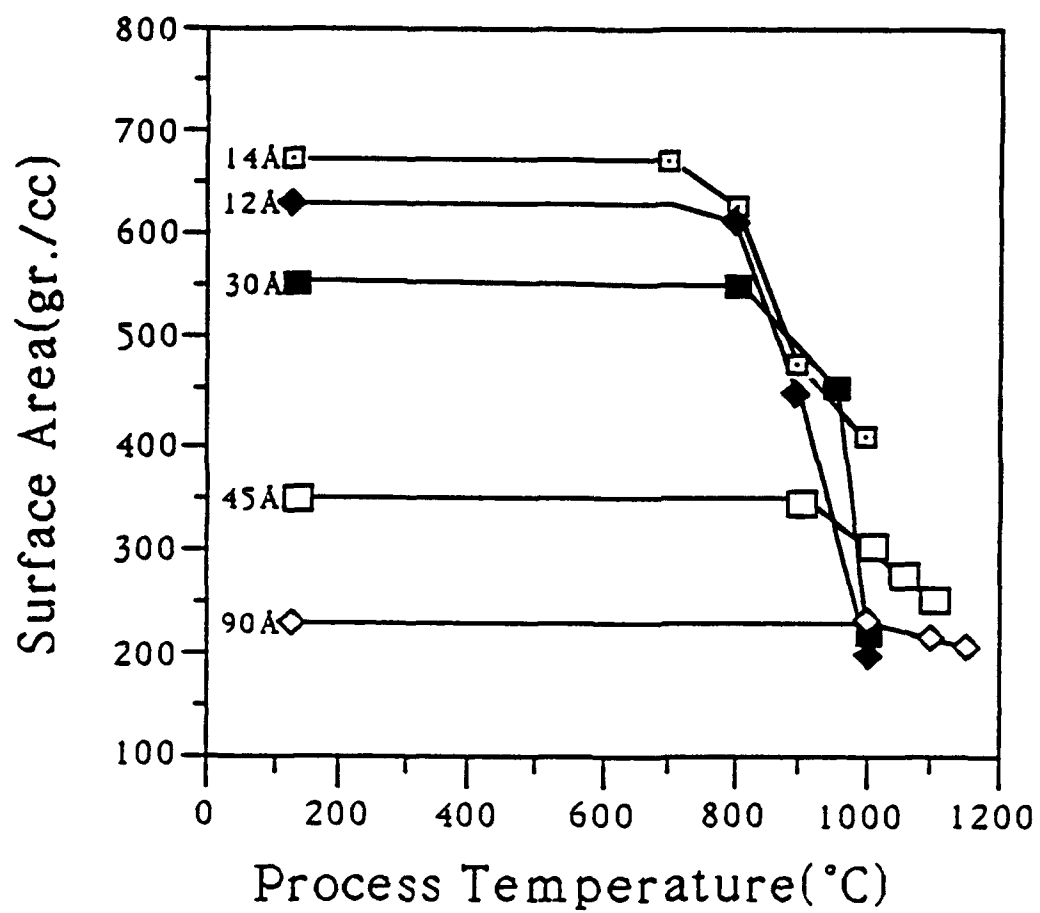


Fig. 5

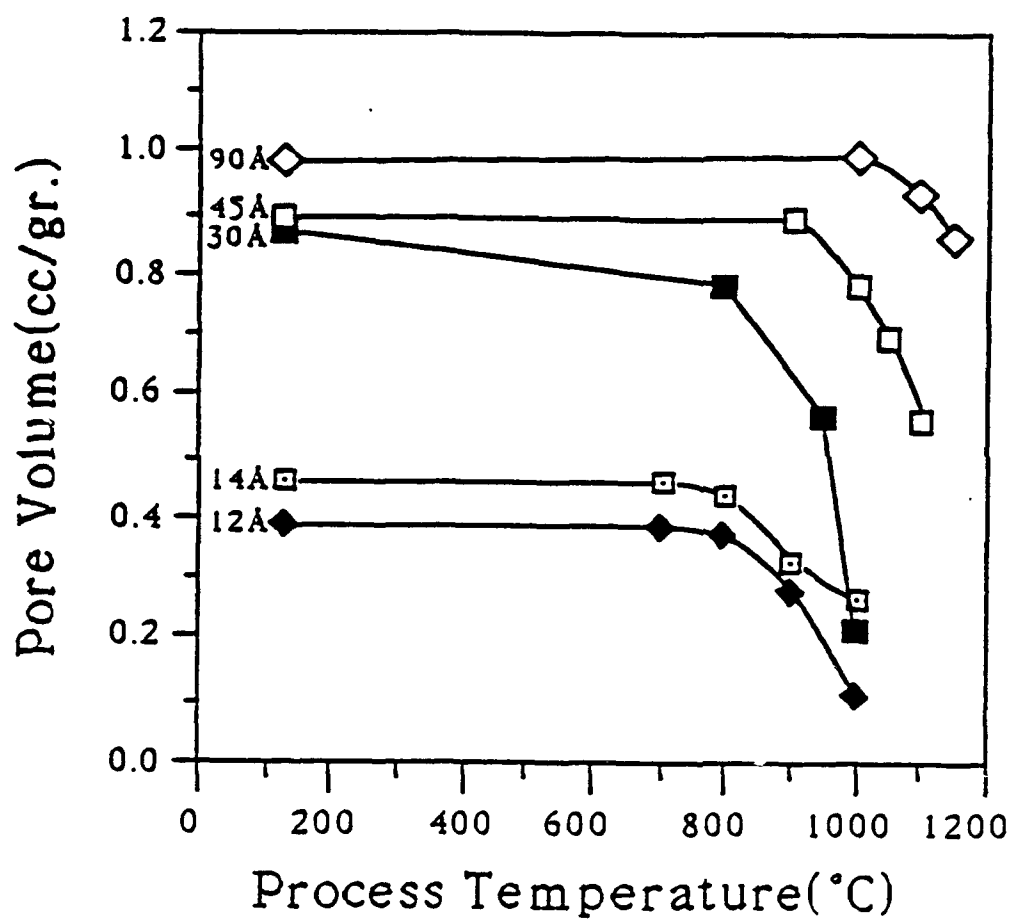


Fig. 6

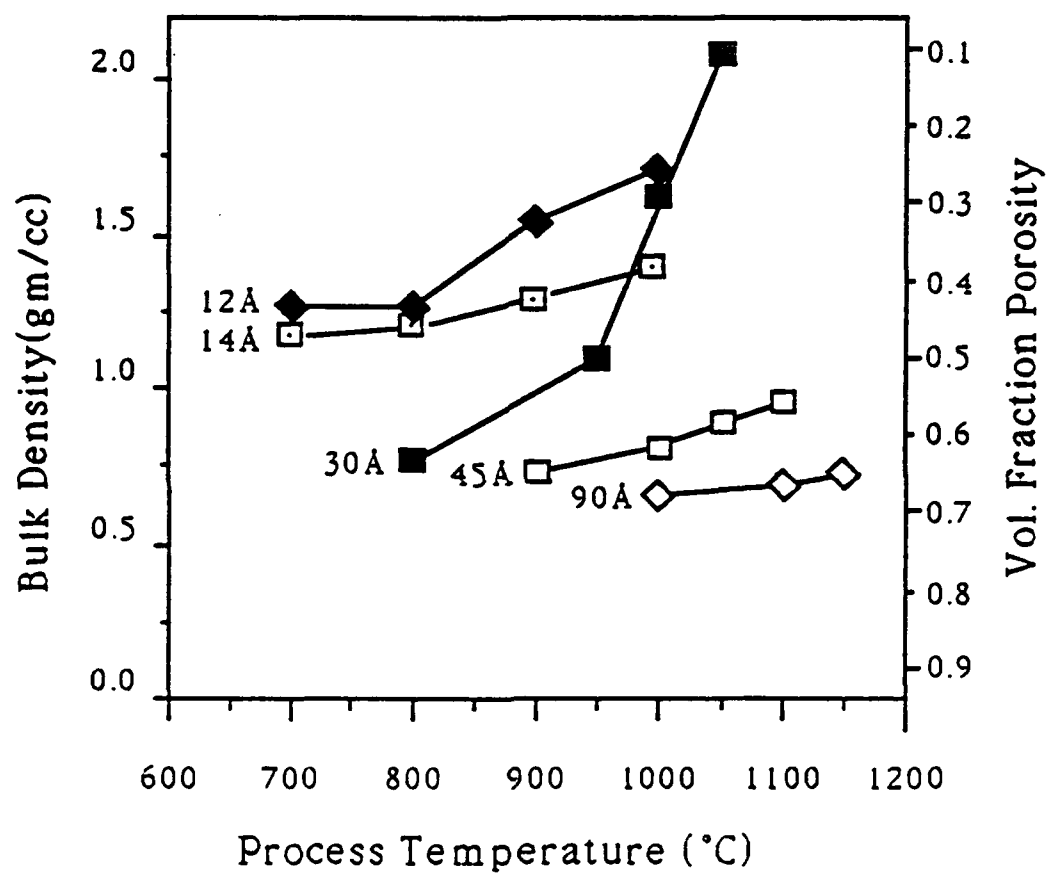


Fig. 7

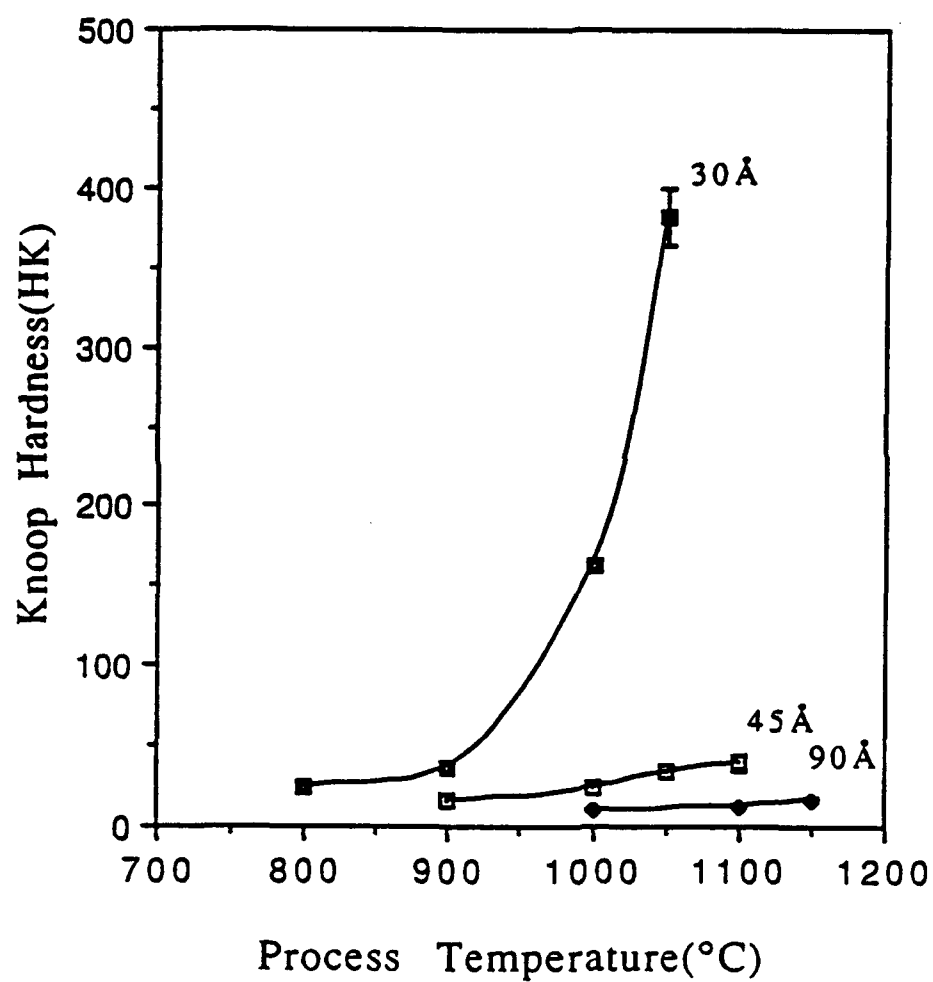


Fig. 8

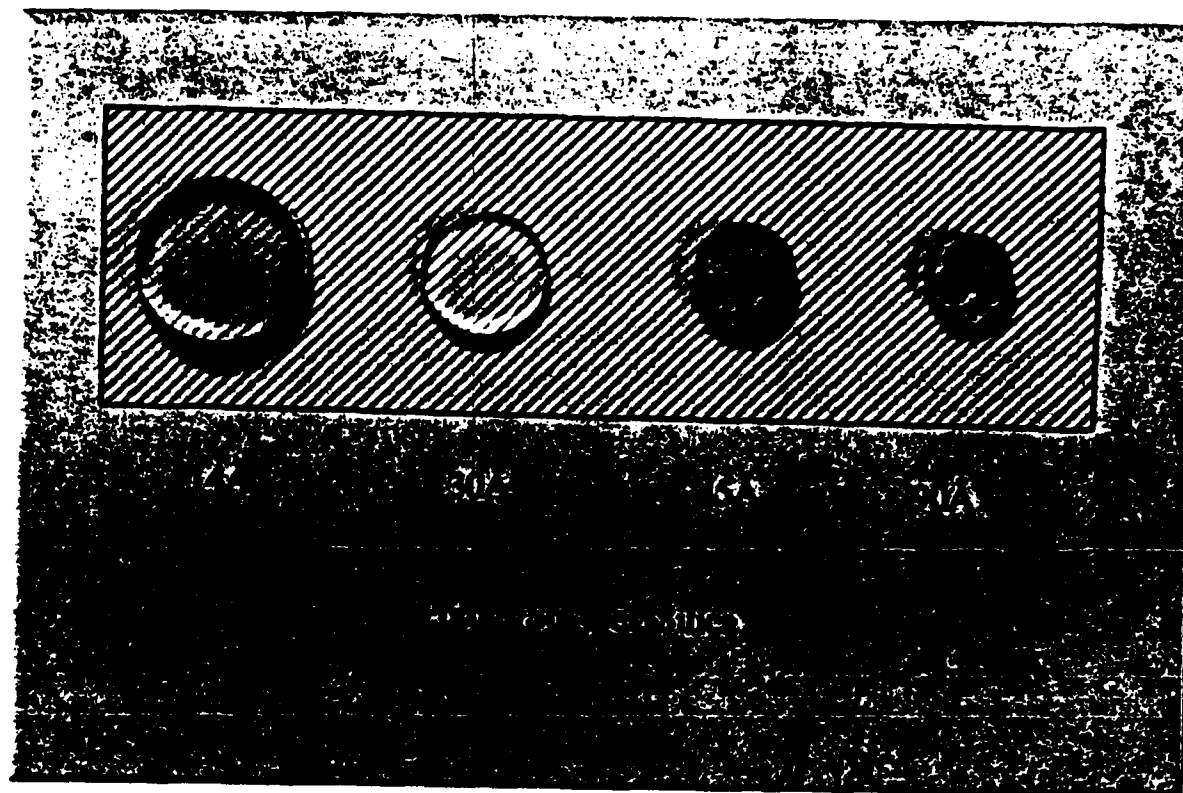


Fig. 9

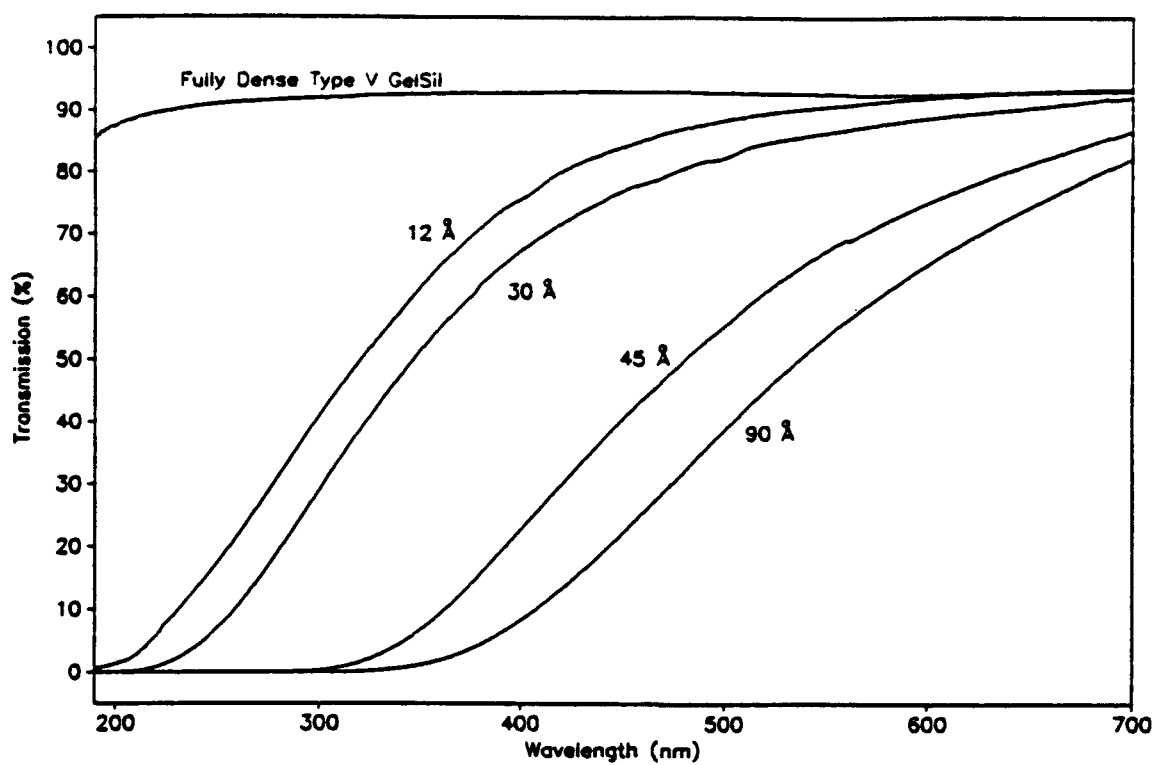


Fig. 10

One-to-Four Gel-Silica Waveguides

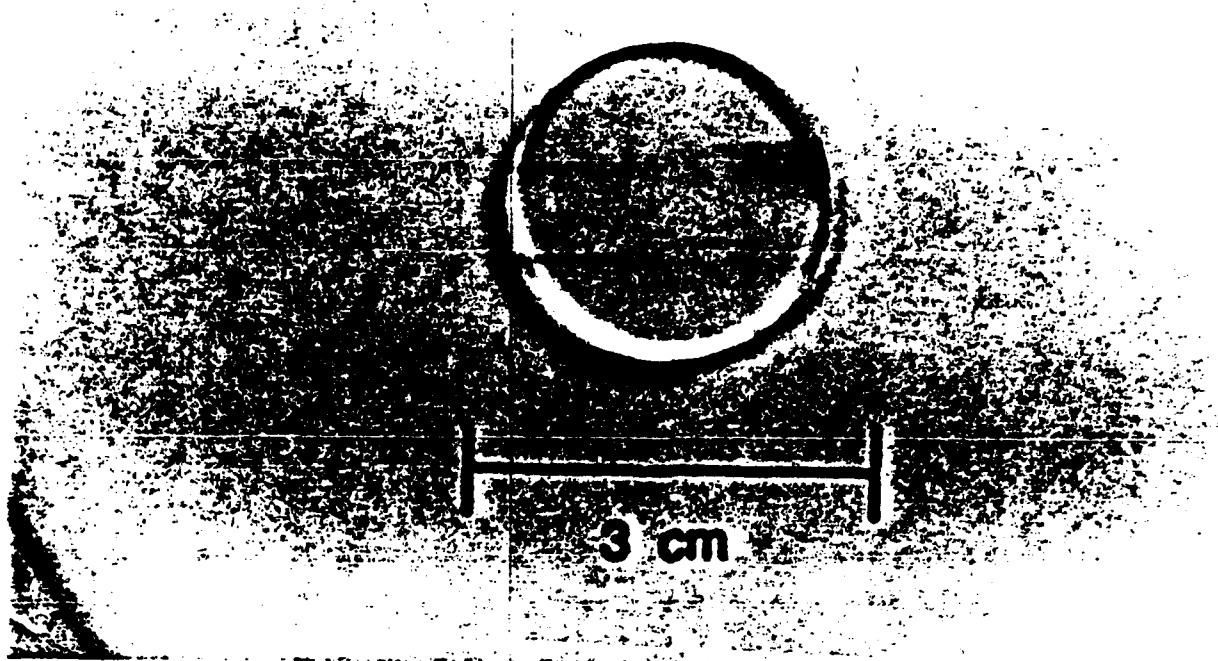


Fig. 11



SECTION III

LASER APPLICATIONS

a. Composite Sol-Gel Glass for Laser and Nonlinear Optical Applications

G.J. Gall, X. Li, T.A. King

(Paper presented at 7th International Workshop on Glasses and Ceramics form Gels, Paris, France, July, 1993).

Abstract

For laser and nonlinear optical applications the sol-gel glass medium can be used effectively as a host matrix for optically active species. However, the porous nature which allows the impregnation of the optical species can also diminish the optical and mechanical strength of the host. Porous glasses are susceptible to preparative conditions, can scatter light and are difficult to polish to optical standards. This poster addresses several important factors which determine the optical characteristics of sol-gel glass composites;

- dopant incorporation using either the pre- or post-doping methods
- dopant homogeneity studied by laser induced fluorescence
- index matching with organic or inorganic species
- optical quality polishing using computer controlled polishing facilities and interferometric analysis.

Pre- or Post-doping?

Both methods of doping sol-gel have advantages and disadvantages;

	ADVANTAGES	DISADVANTAGES
Pre-doping	Molecular immobility Molecular isolation Uniform distribution	Temperature limitations Non densification Poor mechanical strength
Post-doping	Higher densification Tailored matrix	Neo-isolation Temporary location

Preparation of Post-doped Samples

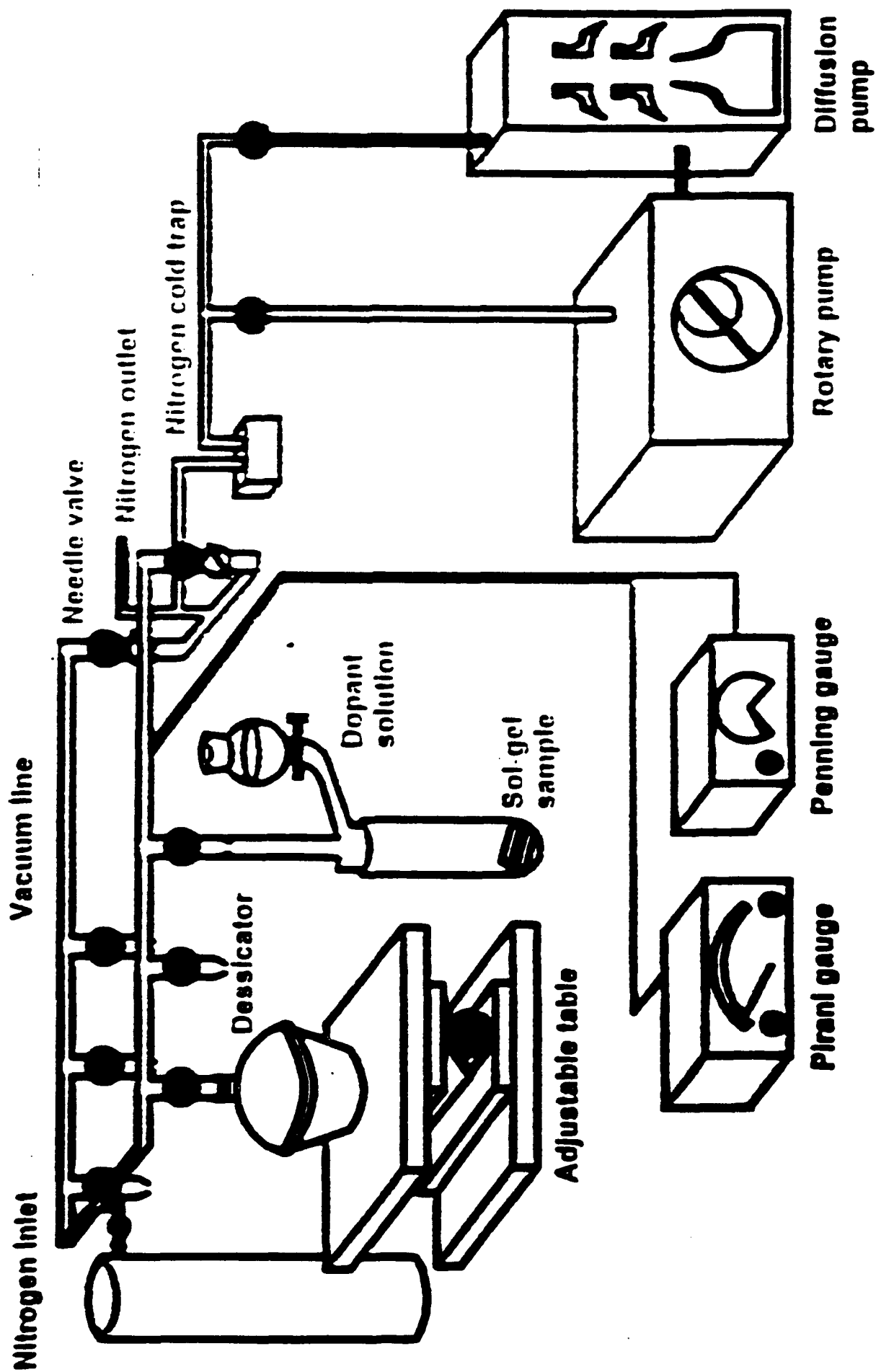
Immersion of sol-gel bulk in solution of optical species under study. Optical species diffuses into sample.

Removal of solvent under hyper-critical drying regime using vacuum drying rig.

Addition of index matching material to reduce scatter losses and close off pores.

Production of optical quality surfaces using conventional polishing techniques.

Vacuum Drying Rig for the Post-doping of Sol-Gel Glasses



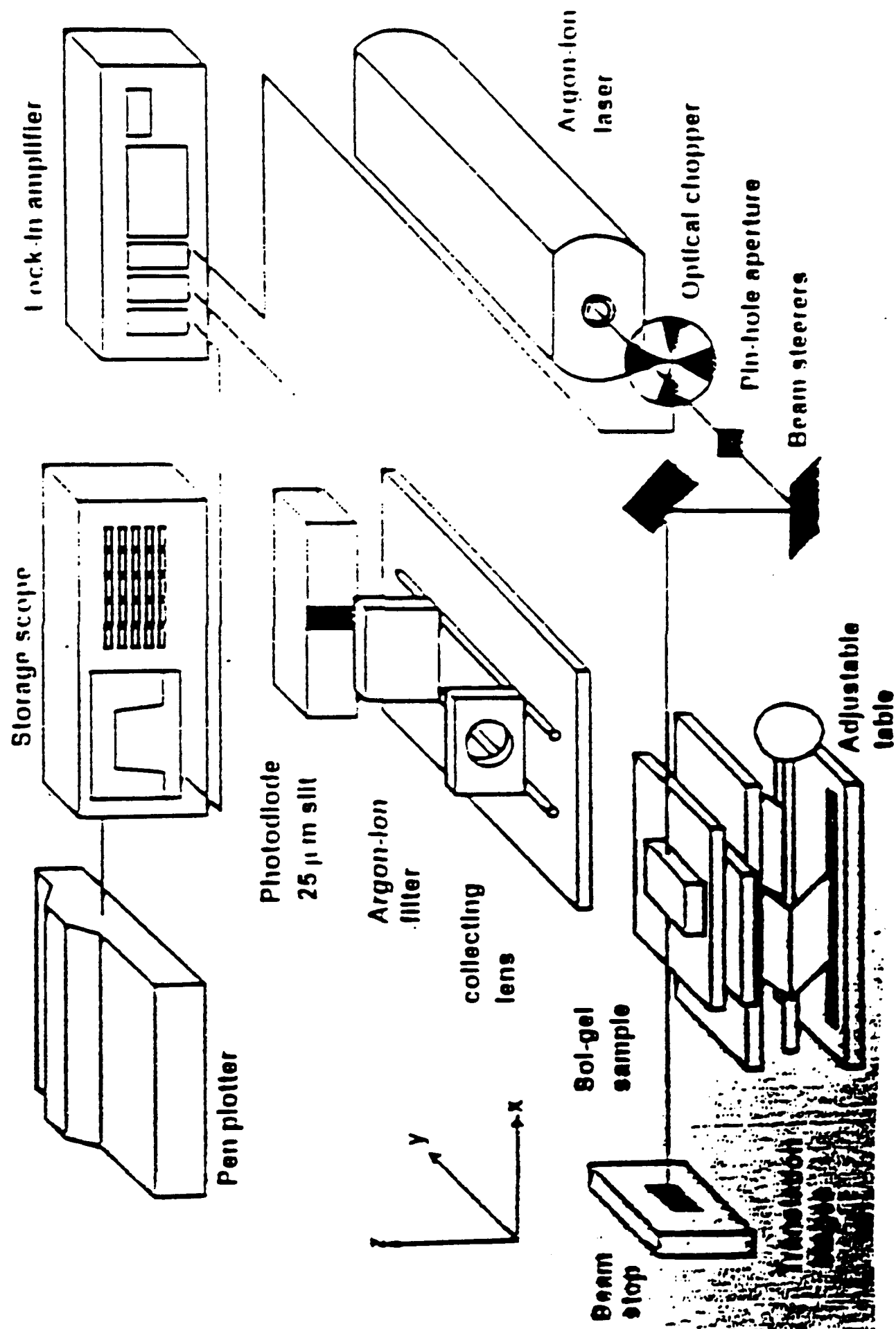
Laser Induced Fluorescence

Laser induced fluorescence is used as a non-invasive technique to assess the homogeneity of the optical species in the sol-gel matrix. Both pre- or post-doping samples can be assessed.

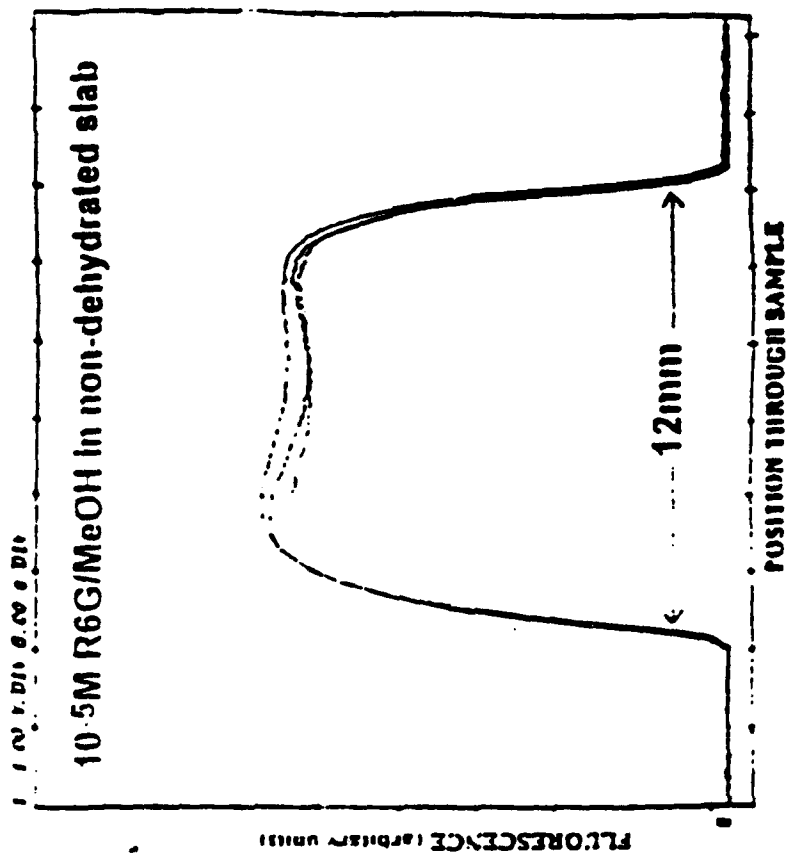
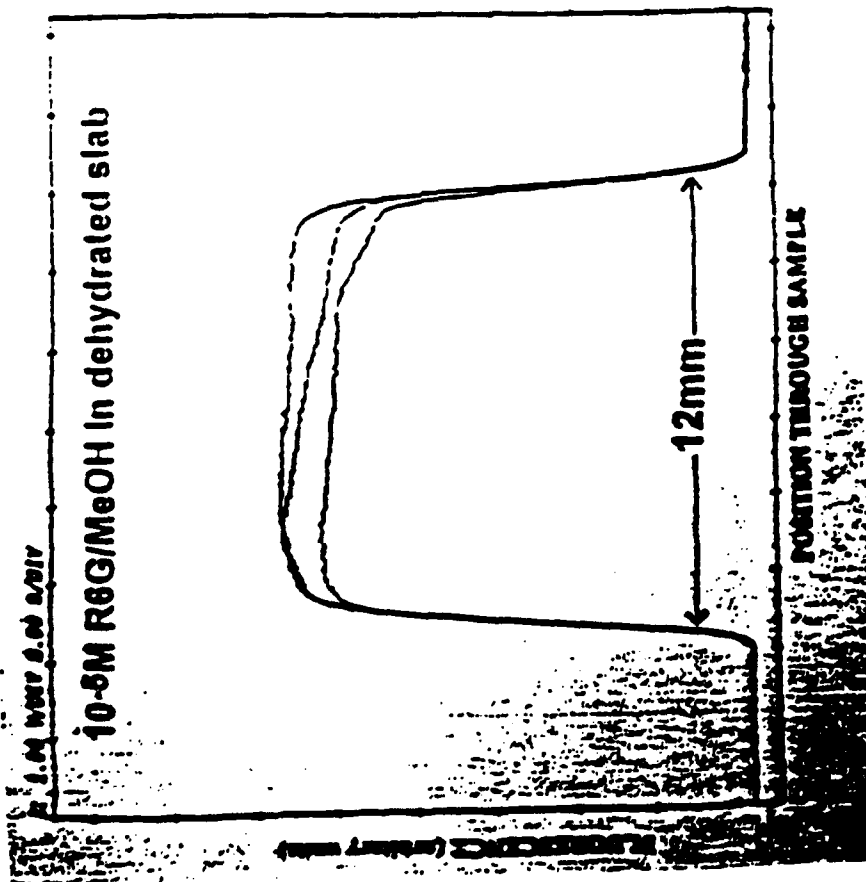
An argon-ion laser with lines between 459nm and 514.5nm is used to excite the dopant molecules.

Pre-dehydration of the samples has a pronounced effect on the homogeneity of the dopant concentration in the sample.

Laser Induced Fluorescence of Organic Dye Doped Sol-Gel Glasses



Dopant Concentration Profiles of Post-doped Sol-Gel Bulks



Index Matching of Composites

Optical losses are incurred from absorption and scatter from the sample. A way to reduce scatter is to index-match the empty pores by filling with an index matching material. This can be polymer such as PMMA, or sol-gel starting materials.

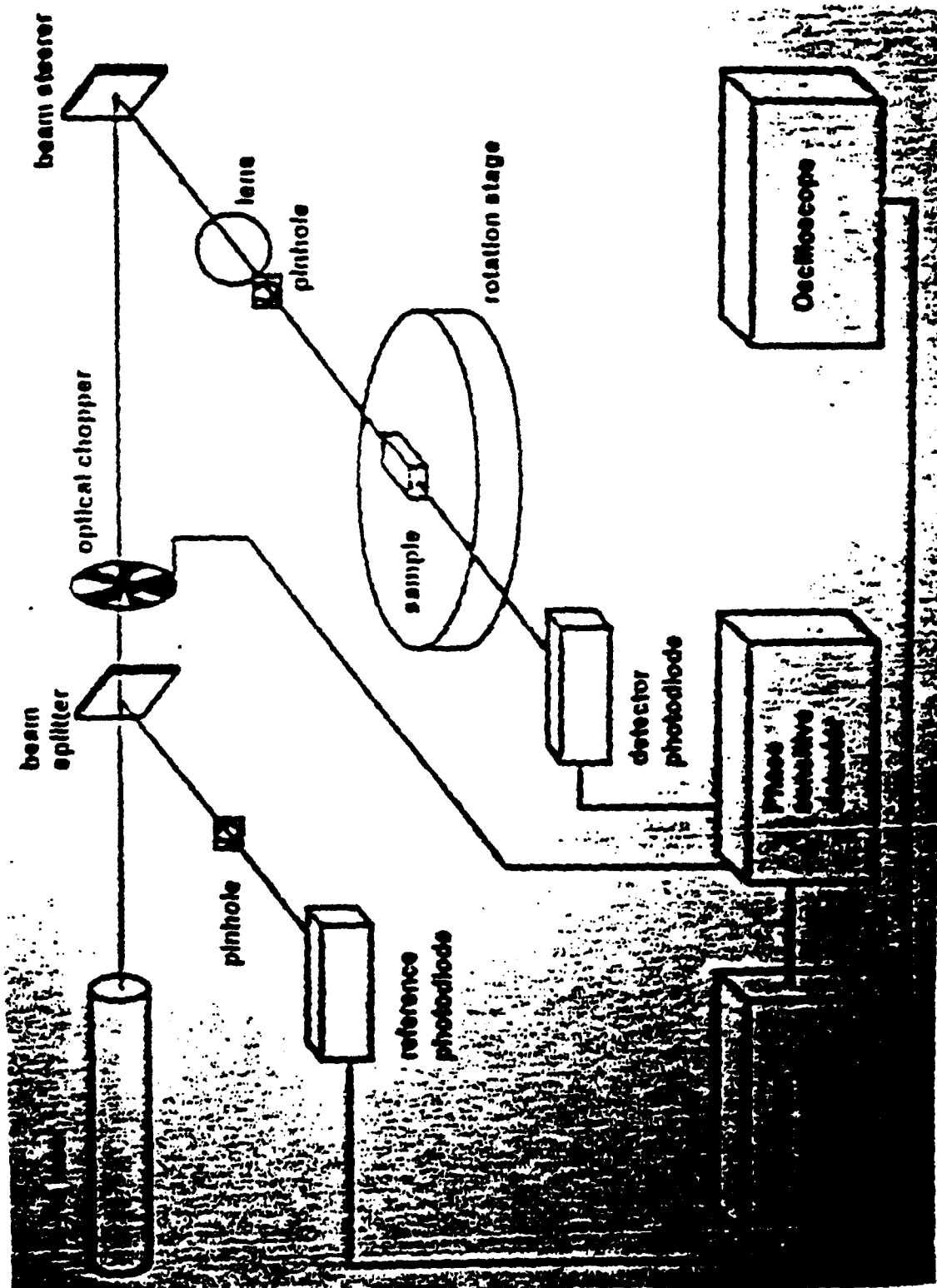
Scatter can occur on at least three spatial levels;

nm scale - from empty pores

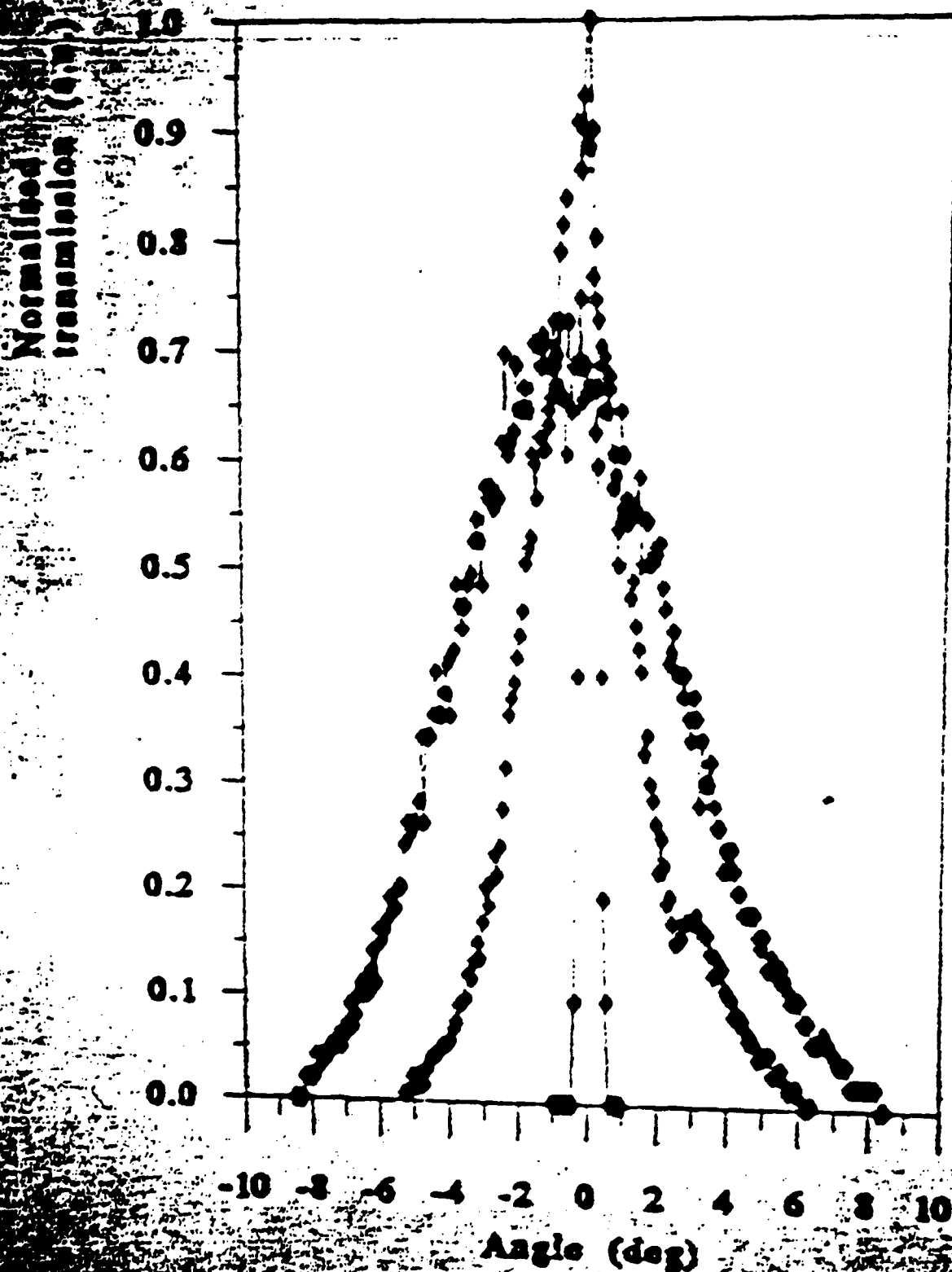
μm scale - from pore clusters

mm scale - from stress induced birefringence, resulting in local refractive index variations.

Forward Scatter/Attenuation Apparatus



- He-Ne Laser
- Sol-Gel/R6G/PMMA 1-6mm
- Sol-Gel/R6G/PMMA 1-16mm



Optical Quality Polishing

The index-matching of the pores with PMMA results in the filling of all surface pores. This removes any problems of unequal capillary pressures due to solvents entering or exiting the matrix. Conventional polishing techniques using a Logitech PS2000 polishing machine have been used to obtain high quality surfaces needed for device application.

Results to date;

Flatness to $\lambda/10$ ($\lambda = 633\text{nm}$)

Surface roughness 2nm

Applications of Sol-Gel Composite Materials

Sol-gel composite materials are readily finding applications due to their processibility. Many devices have been made and continuing interest has led to many devices mentioned below.

Host four lasers, nonlinear organics/polymers/quantum dots.

Passive and active channel waveguides, modulators, switches, interconnects, multiplexers and couplers.

Protective films, optical sensors, detectors and optical fibers.

b. Du Pont Monomer --Porous silica imaging media.

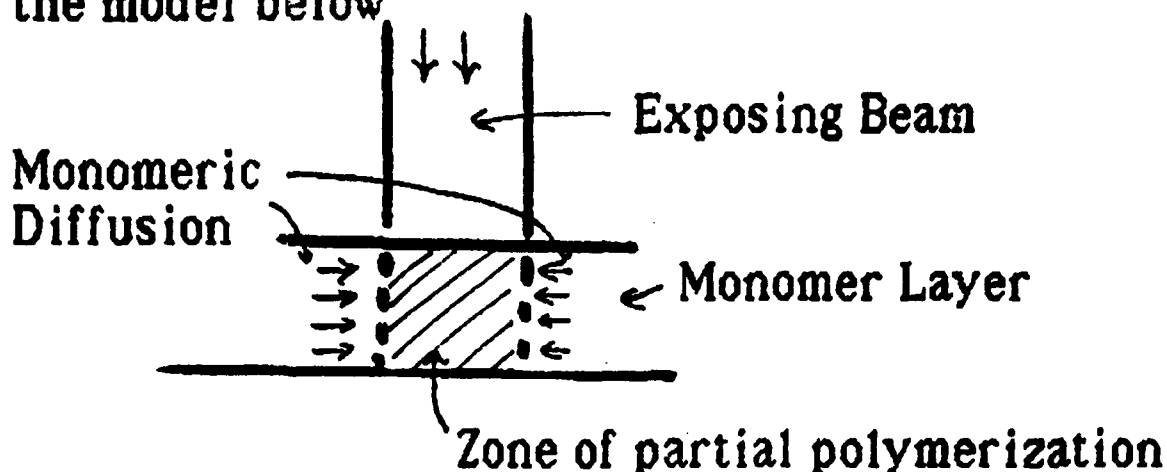
Nicholas J Phillips .

Dept of Physics
Loughborough University
Loughborough
Leicestershire U.K

Summary .

A description is given of a range of optical devices which can be fabricated by the use of novel monomer--porous silica media incorporating the technology of gel-silica and the existing proprietary technology of DU PONT (Wilmington Delaware U.S.A.) With care it should be possible to develop a major new imaging medium with widespread applications in military and consumer optics .

Pores of porous gel silica are filled with DU PONT imaging monomer. The DU PONT monomer acts as in the model below

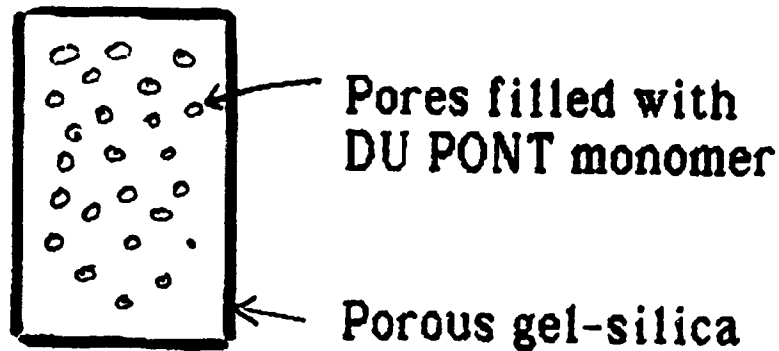


Monomer diffuses to overcome depression of concentration caused by partial polymerization. This results in the creation of a non-uniform refractive index field.



Index modulation is recorded in real-time. Monomer converts to polymer during the recording process. Inter-connected pores in the gel silica enable the diffusion to take place in the silica matrix.

A major issue with DU PONT monomer is that it is sticky and lacks integrity. Thus it needs a skeletal matrix around it, the obvious candidate being porous gel-silica.

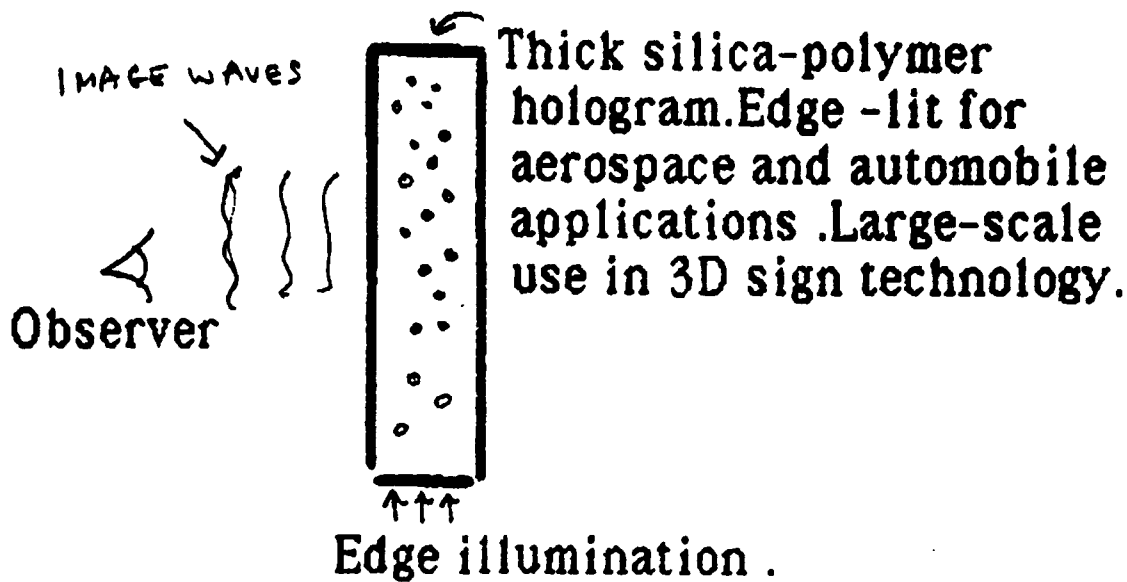


Advantages

- (i) Integrity of monomer structure due to the skeletal framework of silica.
- (ii) Greatly increased fracture strength as compared with pure silica.
- (iii) Resistance to atmospheric attack on embedded monomer.
- (iv) No processing required - real-time recordable.

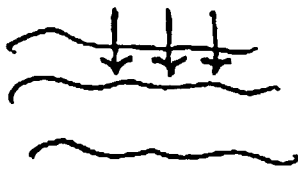
Devices originating from the use of monomer-silica complexes .

1. Thick holograms :



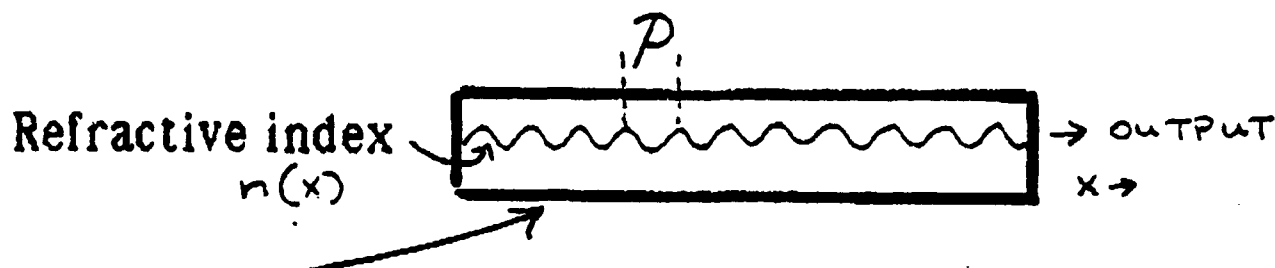
2. Micro-lens arrays .

using existing Loughborough University facility.
(Approx \$1m hardware investment).



U.V Illumination -incoherent
but directional .

3. Distributed feedback laser devices .



Laser dye-monomer-silica matrix.

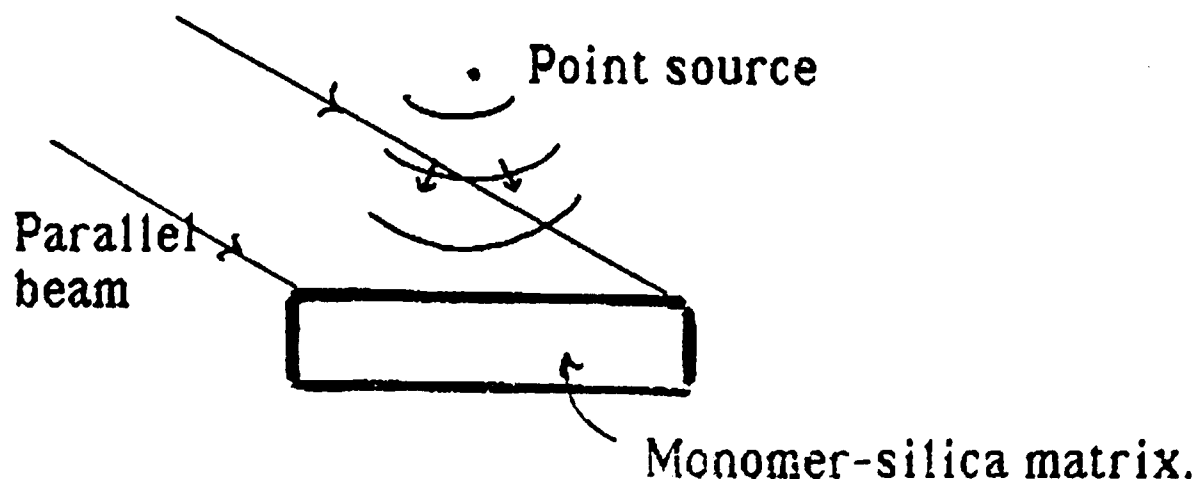
Refractive index has to be spatially periodic with a pitch p of the order of 0.25 microns .

Device must be excited by a pump laser but can be constructed for use at any visible wavelength by choice of dye and control of pitch .

D.F.B.laser is very important in optical communications because of purity of optical output .

4. Optical elements such as diffractive lenses .

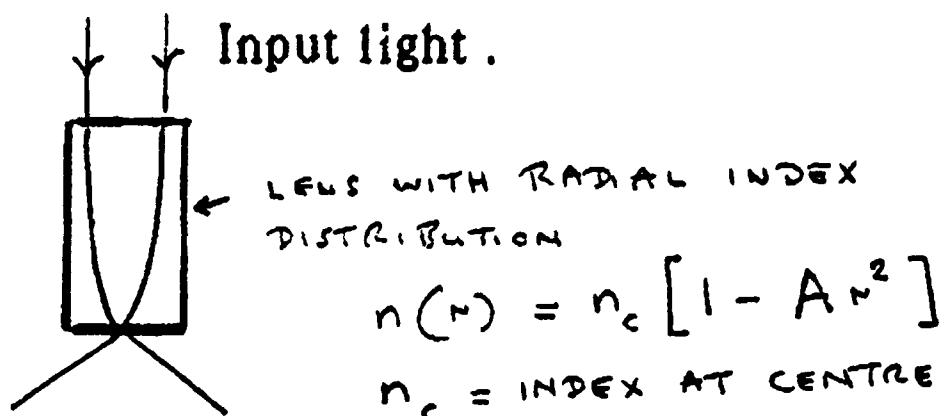
As an example we show an off- axis holographic lens produced by the interference of coherent light.



An important array product :



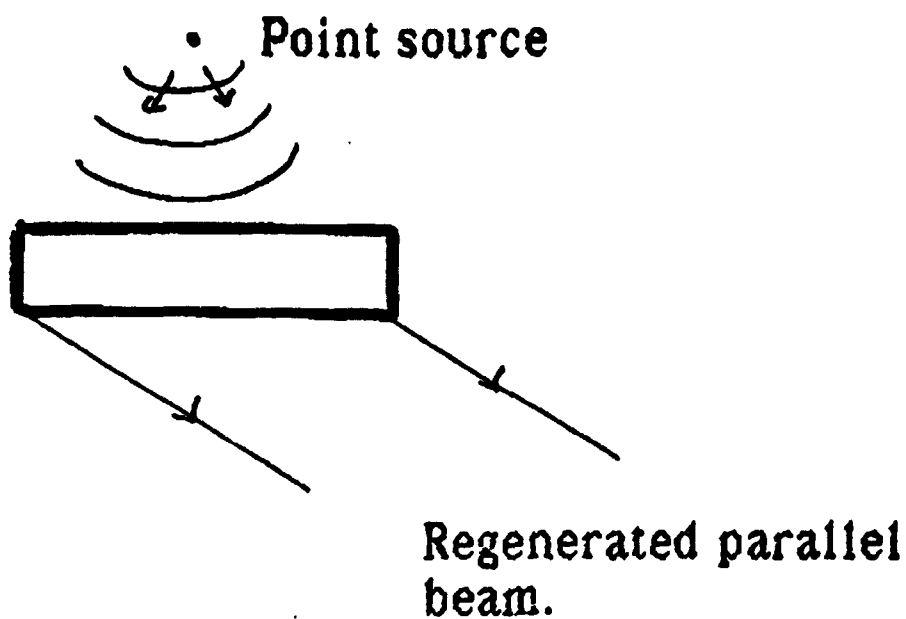
Equivalent to fibre-optic faceplate but orders of magnitude cheaper. Each Grin lens (graded index lens) acts as follows :



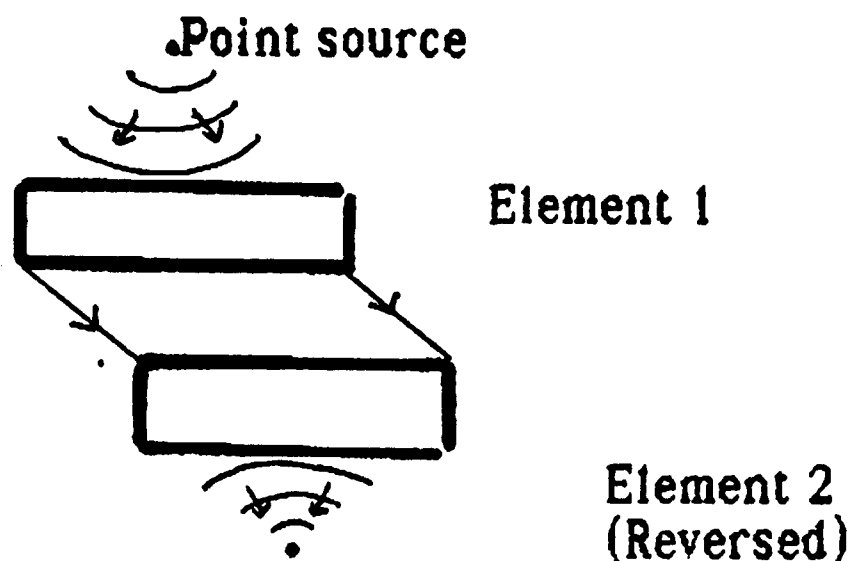
Array useful for display screens especially with the trend towards use of projection (not V.D.U) displays .

Also useful for contrast enhancement in instrumentation ,e.g,cockpit applications .

On replay of the recorded lens we have a typical set-up as follows :



If we replay one element by another , we have the following set-up :



Regenerated focussed
light .

The combined structure formed by 1 and 2 in contact forms a diffractive lens free of transverse chromatic aberration .Our preliminary experiments show that the DU PONT monomer suffers from errors of fringe formation in its raw state thus confirming the need for a skeletal matrix , especially in complex situations as exemplified above .

SECTION IV

SPECTROSCOPY

a. Spectroscopic Studies of Post-Doped Silica Gel Monoliths

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**(Presented at 7th International Workshop on Glasses and Ceramics from Gels,
Paris, France, July 1993)**

Abstract

This paper describes the interfacial molecular interactions of cobalt, Neodymium, Rhodamine 6G and polymethyl methacrylate with silica gel-glass monoliths for samples prepared by the post doping method.

Introduction

Composite gel-glasses can be prepared by one of two routes which require addition of the second phase or dopant at different times during the preparation process. The dopant (inorganic or organic) can be added during the initial mixing stage [1,2] incorporating it homogeneously into the gel as it forms. The other takes advantage of the porous characteristics of the gel and involves impregnating a set, partially densified gel-glass in organic or inorganic media with subsequent chemical reaction (if necessary), drying and sintering where appropriate. The former method is referred to as the pre-doping method and the latter, the post-doping method. Studies presented in this paper relate to materials prepared by the latter route. In the post-doping method, the first step of impregnation is essentially a physical adsorption process. As it occurs in solution, where a range of species coexist (cations, anions, water, organic molecules etc. depending upon the system chosen), an initially impregnated gel-glass is a multi-component system involving surface silanols and the above species. The molecular interactions involved in such systems are expected to be complex. The matter becomes even more complicated when the system undergoes a series of post-doping treatments such as dehydration, rehydration and densification.

In this paper we describe studies on the properties and structures of porous gel-glasses doped with cobalt(II) and Nd(III) salts, Rhodamine 6G and polymethylmethacrylate. A better understanding of the chemistry occurring in such systems will greatly assist in the production of specialist glasses with improved performance characteristics.

Experimental

The method used to prepare metal salt doped complexes is described in reference 3. Samples were analysed 'as prepared', dehydrated, rehydrated and after sintering at 900°C for 8 hours. Rhodamine 6G glasses were prepared using samples which had been outgassed prior to immersion in aqueous solutions containing 5×10^{-6} to 0.01M Rhodamine 6G (Aldrich). Samples were removed from the dye solution after 2 days, dried in air and then water removed on an outgassing rig operating at 5×10^{-2} atm pressure for at least 24 hours prior to spectral analysis. Fully polymerised polymethylmethacrylate/ gel-glass composites were prepared using a methyl methacrylate which had been freed of inhibitor by washing with a 5% NaOH/ 20% NaCl solution followed by repeated washing with distilled water [4] The monomer was dried overnight with anhydrous sodium sulphate and left for 48 hours over a 4 Å molecular sieve. The dried MMA was redistilled under reduced pressure immediately prior to use. In order to ensure efficient impregnation of the gels by the methyl methacrylate samples were outgassed for 48 hours at a pressure of 5×10^{-2} atm before being immersed in a neat solution of MMA which had been catalysed for polymerisation by the addition of 2% benzoyl peroxide. After soaking overnight, samples were transferred to a 1:1 solution of MMA (catalysed for polymerisation by the addition of 0.5% benzoyl peroxide) and carbon tetrachloride. The subsequent polymerisation was carried out at 60°C in sealed containers. Samples were left for 48 hours before removal and cleaning prior to spectroscopic analysis.

All spectroscopic analysis (FTIR, FTIR, NIR, UV/VIS) was performed using instruments available in the Chemistry Department at Brunel University.

Cobalt and neodymium doped gel-glasses

A series of metal salts (nitrates, chlorides and acetates) were used to impregnate partially densified gel-glasses in order to investigate the ability of silanol groups to compete with water molecules and the available counter ions for the first coordination sphere of the metal ion dopants. The coordination chemistry of the metal ions was found to depend upon the nature of the anions, and the thermal history of the glass. For the cobalt system pink, purple, pale mauve and blue glasses could be produced. For the as prepared glasses only acetate ions were able to compete with water as a ligand for the cobalt ion. Upon dehydration, all three anions were able to compete effectively with water as ligands for the cobalt ions. Figure 1 shows the structures suggested from the UV/VIS study and associated EXAFS measurements [3] for the nitrate doped sample. . The acetate and chloride doped samples have cobalt in coordination environments similar to that found in crystals of salts. For the nitrate doped samples this is not the case. When all three samples are sintered at 900°C identical glasses are produced in which silanol oxygen atoms function as ligands for the metal ions. Spectra obtained, Figure 2 indicates that both octahedral and tetrahedral coordination geometries are observed in the sintered glass. Although both large and small pore glasses have been investigated, it must be noted that the most dramatic changes in coordination chemistry have been observed for narrow pore glasses. Associated NIR spectroscopic studies has shown that adsorbed metal ions and counter ions promote further hydration of the gel-glass surface. Depending on the basicity of the anions, these may also interact with surface Si-OH groups through hydrogen bonding. The decreasing order of efficiency of the anions in promoting water aggregation is nitrate> chloride> acetate which can be correlated with the ability of the anions to replace water in the first coordination sphere of cobalt ions.

Neodymium(III) doped glasses have been prepared from salts of the chloride and nitrate. The hypersensitive bands arising from the transitions $^4I_{9/2} \rightarrow ^4G_{5/2}$ and $^4I_{9/2} \rightarrow ^2G_{7/2}$ at 575 and 580nm respectively show the most significant changes after dehydration and sintering. Spectra for the neodymium nitrate doped glasses are shown

in Figure 3. The hypersensitive bands are better resolved on dehydration and are much increased in intensity. The spectral changes are related to the formation of an inner-sphere, low symmetry species where more basic (than water) nitrate ions are involved in the first coordination sphere around the metal ion, similar to that observed for the cobalt doped glasses. On sintering at 900°C, the bands due to the hypersensitive transitions are red shifted by ca. 4 cm^{-1} and reduced in intensity. The observed red shift indicates that the Nd-O interaction has a higher degree of covalency than for the as prepared gel-glasses, however the coordination environment is not fully known. It is suggested that the neodymium ions are at least six coordinate.

Rhodamine 6G doped Glasses

The addition of Rhodamine 6G to gel glasses thermally treated at 800°C results in orange glasses which fluoresce. In large pore samples (pore radius ca. 40Å) fluorescence spectroscopy has shown that RG6 molecules are not trapped in silica glass cages as has been found for materials prepared by the sol to gel method [5]. FTIRMAN spectroscopy has shown that the carbonyl groups of the RG6 molecule are involved in hydrogen bonding (band at ca. 1720 cm^{-1} due to C=O stretch [6] is broader and shifted to lower wavenumber on incorporation into the gel-glass matrix),

Figure 4. The presence of the dye in the glass significantly reduces the amount of water present within the gel glass and the uv/visible spectrum of the adsorbed dye remains unaltered on dehydration. A comparison of dye doped and blank glasses treated in an identical fashion (except for incorporation of the dye) show that hydration takes much longer to accomplish for the dye doped glass, Figure 5. The pattern of water speciation is different from that observed for blank glasses. The majority of water present in the glass during the early stages of hydration is monomeric and bound only to silanol groups rather than being hydrogen bonded to other water molecules. The dye molecule is hydrogen bonded to the surface and as such appears to minimise hydrogen bonding between water molecules. It is thought that this phenomenon may have a considerable role to play in determining the stability of organic/ inorganic gel composites for use in tunable lasers, for example.

Spectroscopic studies of MMA and PMMA impregnated gels

NIR and FTRAMAN spectroscopy have been successfully used to monitor the MMA to PMMA transformation. Bands of specific interest [7] in understanding how the gel matrix interacts with the polymer network are the carbonyl absorption frequency at ca. 1730 cm^{-1} and the carbon-carbon double bond ($>\text{C}=\text{C}<$) vibration which occurs at ca. 1630 cm^{-1} . Although the silica network also has a Raman spectrum it is very weak in relation to that derived from the organic material and thus hardly affects the spectra obtained. Spectra obtained from unpolymerised MMA (containing 2% benzoyl peroxide) and MMA impregnated gels are virtually identical although a shoulder is observed on the low wavenumber side of the carbonyl absorption band indicating that the gel surface interacts with the MMA. After polymerisation, the band arising from the carbonyl group is shifted to higher wave number which is the result of a loss of α , β -unsaturation in the monomer on polymerisation. A small shoulder on the low wavenumber side of this band (in comparison to that observed for PMMA only) suggests that some interaction between the gel network and the polymer network exists. The band arising from the presence of carbon-carbon double bonds at ca. 1640 cm^{-1} disappears indicating that the MMA has fully polymerised, Figure 6. Confirmatory data was obtained from NIR studies where the disappearance of a band at ca. 1600nm due to $\text{H}_2\text{C}=\text{}$ groups [8,9] on polymerisation suggested that PMMA was formed inside the gel. The Raman data suggest that there is a stronger interaction between the monomer and the silica gel than the polymer and the silica gel. If gels were prepared by a one step impregnation process as other authors have recommended then the conversion of monomer to polymer was never complete. The two stage impregnation process led to non-porous gels with good optical clarity which were fully polymerised.

Conclusions

These studies have shown the importance of surface interactions in the formation of doped gel-glasses. It is clear that within small pores (eg. 1.2nm radius) that interactions between surface species such as silanols and the guest ions or molecules

are critically important in determining the final optical properties of the gel composite.

References

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Figure Legends

- (1) Scheme based upon UV/VIS and EXAFS measurements for the likely coordination environments of dehydrated cobalt nitrate, chloride and acetate doped glasses.
- (2) UV/VIS absorbance spectrum of a sintered cobalt nitrate doped sample
- (3) UV/VIS reflectance spectrum of neodymium nitrate doped samples (a) as prepared, (b) dehydrated and (c) sintered
- (4) FTRAMAN spectrum of Rhodamine 6G doped glass (top trace) and Rhodamine 6G (bottom trace)
- (5) Reflectance NIR spectra of the second overtone region of a blank silica glass (hydrated (d) and dehydrated (c) and a rhodamine 6G doped glass (hydrated (b) and dehydrated (a)). S_n' corresponds to water molecules only hydrogen

bonded to surface silanol groups and $S_{1'}$ to water molecules which are hydrogen bonded to surface silanols and partially to other water molecules.

- (6) FTRAMAN spectra of (a) a MMA impregnated gel glass and (b) a PMMA impregnated gel glass. Note the complete absence of the band at ca. 1640 cm^{-1} arising from the carbon-carbon double bond.

CCH 13/7/1993

